# PHOSPHORUS SPATIAL DISTRIBUTION, SORPTION, AND TRANSPORT IN A SPODOSOL

By

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# PHOSPHORUS SPATIAL DISTRIBUTION, SORPTION, AND TRANSPORT IN A SPODOSOL

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Large loads of phosphorus (P) enter Lake Okeechobee from the watershed to the north. These large influxes of P could trigger accelerated eutrophication of this lake. Dairy farming land-use has been identified as the primary source of this P. Little information has been reported about the effect of soils within the watershed, mainly Spodosols, upon P movement into streams. One objective of this research was to determine concentrations of P in soil profiles affected by dairy farming and the P retention capacities of those soils. A second objective was to investigate factors that affect the P sorption kinetics and P transport through the spodic horizons.

In order to investigate the effect of dairy farming upon the P status and sorption capacity of the soils, soil samples were collected at different depths and distances along transects for selected dairies. Transects between milking barns and the closest water course for each of the three dairies were used to determine spatial distribution of P in the soil. The three extractable forms of P (water, Mehlich I, and total) were influenced by past and present land use, i.e., pasture vs high intensity animal land-use areas, physiographic and animal use patterns, and P sorption (adsorption + precipitation) of each horizon.

Stirred aqueous suspensions of soil samples were employed to measure the effect of initial P concentration ($C_0$) and the soil solids mass upon kinetics of P sorption. Increasing the $C_0$ and contact time, and decreasing the soil solids mass were observed to increase the amount of P sorbed. All of the data (by time, $C_0$, and soil solids mass) were approximately described by a single nonlinear Freundlich sorption isotherm.

The transport of P with water flow was determined by displacing wide pulses of aqueous electrolyte solutions containing given P concentrations through short soil columns. The relative amount of P sorbed (net sorbed/total applied) increased with decreasing $C_0$ which reflects the nonlinear relationship between sorbed and solution phases. The shape of the sorption breakthrough curve was influenced by $C_0$.

# CHAPTER I
# INTRODUCTION AND SYNTHESIS OF PUBLISHED LITERATURE

## Background Information

Over the past 20 years, the Taylor Creek/Nubbin Slough (TCNS) watershed and the Lower Kissimmee River Valley have developed into a major agricultural area with emphasis on dairy farming, beef cattle, and citrus. A study by Federico et al. (1981) concerning the eutrophication of Lake Okeechobee shows that the TCNS watershed (on an annual basis) contributes about 30% of the phosphorus (P) to the lake while contributing only 4% of the total water budget. The nutrient enrichment of this watershed has been identified as a result of both agricultural point and non-point sources pollution, primarily from dairy operations within the basin (Ritter and Allen, 1982). Non-point sources are generally runoff from grazing pastures and dairy staging areas near milking barns. Data from selected stream channels in the TCNS basin showed ranges of total P concentration from 1.7 to 4.7 mg/l and 0.41 to 1.22 mg/l for dairies and pasture lands, respectively (Allen et al., 1982). Their data also showed that 90% of the total P in aqueous solution is in inorganic form (ortho-P). The concentration of P in the rain water and in Lake Okeechobee is 0.1 mg/l (Allen, 1988). Most phosphorus (approximately 70%) in animal manure is in inorganic form (Overcash et al., 1983) and the organic P is subject to transformation to ortho-P. As a simplification, only the behavior and transport of the ortho-P ion is considered in this dissertation.

The relationship of geology and soils in Okeechobee County was studied by Rowland and Fiskell (1970). The two major geologic formations exposed in Okeechobee County are Caloosahatchee and Fort Thompson formations of Pleistocene age (McCollum and Pendleton, 1971). Superimposed upon these two geological formations are the marine terraces. The soil surface ranges in elevation from 4.3 m above msl (mean sea level) near the Lake to 22.9 m above msl in the North Central part. In the latter area, alkaline soils were formed from freshwater marl while, at lower elevations, other soils were influenced by the salt-water marl (Rowland and Fiskell, 1970). Approximately 65% of the soils in Okeechobee County are Spodosols. Spodosols are mineral soils that have a subsurface horizon in which active, amorphous organic-sesquioxide materials have accumulated (Soil Survey Staff, 1975). Of those Spodosols, 48% are classified as Myakka soil series and 40% Immokalee soil series (McCollum and Pendleton, 1971). Both of these soils are deep, poorly drained Haplaquods formed from marine deposits. These soils have rapid permeability in the A horizon and the topographic slope ranges from 0 to 2%. The Bh horizon depth ranges from 50 to 76 cm (20 to 30 in) for the Myakka soil series , and from 76 to 102 cm (30 to 40 in) for the Immokalee soil series.

Mineralogical characteristics of Florida Haplaquods were studied by Zelazny and Carlisle (1971), and Harris and Carlisle (1987). The particle size distribution on a weight basis was predominantly sand, with clay accounting for less than 5%. The mineralogical analysis of the A and E horizon clay fraction contained quartz, kaolinite, and hydroxy-interlayer minerals. The mineralogical analysis of the Bh and C horizon clay fraction showed the presence of quartz, hydroxy-interlayer minerals, kaolinite, and gibbsite. Non-crystalline materials were found in the A, Bh, and C horizons. Some chemical characteristics of Haplaquods were investigated by Calhoun and Carlisle (1974) and Yuan (1966). The pH of the Haplaquods were slightly acid, between 4 and 6. The range of organic matter content, extractable bases, cation exchange capacity, and base saturation values was approximately the same for A and Bh horizons, and larger than for the E horizons (Calhoun and Carlisle, 1974). The organic matter content was found to be related to the pH, moisture equivalent, cation exchange capacity, and C:N ratio (Yuan, 1966). The translocated and chemically active components in Spodosols consist mostly of poorly crystalline aluminum (amorphous) and iron oxides and Al-Fe-organo complexes (Allen and Famming, 1983). The amorphous material in the spodic horizon was characterized by a high alumina and low silica content (Yuan, 1969). Furthermore, aluminum is the dominant cation and the exchange properties of the spodic horizons are dominated by Al and organic carbon complexes (Holzhey et al., 1975).

## Phosphorus Reactions in Acid Sandy Soils

Although phosphorus occurs in nature as both organic and inorganic forms, P in soil-water systems occurs predominantly as ortho-phosphate. Reviews of organic forms of soil P transport in soils, and transformation between organic and inorganic forms are given by Dalal (1977) and Stevenson (1982). The ortho-phosphoric acid ($H_3PO_4$) dissociates stepwise in aqueous systems, releasing protons as pH increases. The $H_2PO_4^-$ and $HPO_4^{2-}$ ions are the predominant species that can be expected to take part in phosphate sorption reactions in the soil solution of most agricultural soils in the pH range of 4.0 to 8.5 (Berkheiser et al., 1980).

Phosphorus transport with water flow in soil profiles depends heavily upon the reaction with soil materials and their phosphorus-retention capacities. Phosphorus retention capacities have been shown (Ballard and Fiskell, 1974) to be significantly correlated to such soil properties as clay and silt content, pH and loss on ignition (representing organic matter content), but the relationship was indirect through association with extractable Al. Regardless of the extractant used, extractable Al and Fe correlated significantly with P retention, and the contribution to P retention per unit of extractable Al or Fe varied with the forms of Al and Fe in soils and their solubilities in different extractants (Yuan and Breland, 1969). However, per unit weight basis, the order of activity in P retention was exchangeable > amorphous > crystalline with apparently little distinction between Al and Fe within these categories (Ballard and Fiskell, 1974). The greater contribution of Al to P retention was primarily a function of the greater amount of Al compared to Fe in active forms (Ballard and Fiskell, 1974). The reactions of P in soil are of two kinds: the precipitation of sparingly soluble phosphate salts and the adsorption of phosphate on the surfaces of soil particles (Larsen, 1967).

Lindsay (1979) provided an extensive compilation of possible phosphate minerals formed in soils. For acid soils, he inferred that precipitation/dissolution processes were controlled by aluminum and iron minerals. Aluminum is a major constituent in soils and forms a number of insoluble phosphate minerals (Lindsay, 1979). However, the presence of any given phosphate mineral in soil is difficult to verify by X-ray diffraction since these compounds either occur in small quantities (Haseman et al., 1950) or are amorphous in nature (Lindsay et al., 1962). It was suggested that amorphous ferric and aluminum phosphates were important initial reaction products in soil receiving high P applications and that these compounds were considered to crystallize slowly (Lindsay et al., 1962). Furthermore, those amorphous materials were 10 to 30 times more soluble than the crystalline counterpart.

Ortho-P is adsorbed onto mineral surfaces by a ligand exchange reaction (Hingston, 1981; Mott, 1981; Parfitt, 1978). Surface complexes resulting from ligand exchange contain no water molecules between the surface Lewis acid site and the adsorbed P (inner-sphere complex). A review of ortho-P adsorption by ligand exchange has been presented recently by Goldberg and Sposito (1985). They presented indirect evidence (i.e., kinetics of adsorption and desorption, hydroxyl ion release, infrared spectroscopy, and stereochemical calculations) in favor of ligand exchange reaction as the mechanism of the ortho-P and surface hydroxyl reaction. However, the nature of the coordination of the adsorbed phosphate ion on the hydroxyoxide mineral, e.g., monodentate vs bidentate, has not been resolved (Goldberg and Sposito, 1985). The amount of P sorbed by the soil or soil materials is affected by changes of the physical and chemical conditions during the reaction experiments (Syers and Iskandar, 1981; Berkheiser et al., 1980). In general, the important factors affecting P sorption-desorption are as follows: (1) amount and nature of soil components, (2) pH, (3) other ions (cations and anions, inorganic or organic), (4) kinetics, and (5) degree of saturation of the sorption complexes.

Generally, precipitation and adsorption processes proceed simultaneously in the soil system. Both of these reactions involve the formation of strong chemical bonds and similar bonding mechanisms (Corey, 1981; Hsu, 1965). They differ primarily in geometry, adsorption being two-dimensional and precipitation three-dimensional (Corey, 1981). Because of the difficulty distinguishing between these two processes, the "catch all" term "sorption," which includes adsorption and precipitation type reactions as well as any mechanism which tends to transfer P from the solution phase to the sorbed phase in the soil, will be used throughout this dissertation. Kinetic experiments have been used to distinguish phosphate adsorption from precipitation.

Reaction of P in the solution with the soil occurs as a fast initial reaction, i.e., completed within seconds, minutes, or hours, followed by a much slower reaction, i.e., completed within days, months, or years. This behavior of ortho-P reaction in soil and soil materials has been documented since the 1950s (Low and Black, 1950). Excellent reviews about phosphorus reaction with soil materials have been published by Parfitt (1978), and Syers and Iskandar (1981). The initial fast reaction is commonly recognized to occur between exposed Al-OH and Fe-OH surface groups and ortho-P (ligand exchange). However, different explanations have been given for the slow reaction mechanisms. One of the interpretations of the slow reaction has been that the rate-limiting step could be the precipitation- (van Riemsdijk and Hann, 1981; Veith and Sposito, 1977; Chen et al., 1973; Hsu, 1965) or diffusion-controlled process (van der Zee et al., 1986; van Riemsdijk et al., 1984; Kuo and Lotse, 1973).

Studies of ortho-P sorption by aluminum and iron hydroxides were conducted by Hsu (1965). He concluded that (1) precipitation and adsorption result from the same chemical force, (2) whether precipitation or adsorption occurs is dependent upon the form of aluminum and/or iron present at the moment of the reaction, and (3) surface-reactive amorphous aluminum hydroxides and iron oxides dominate the process of phosphate sorption in soil. Kinetic studies of ortho-P sorption by aluminum hydroxide (Chen et al., 1973) and iron oxide (Ryden et al., 1977) also showed an initially rapid decrease in solution P concentration (less than 24 h) followed by a much slower one which continued through the period of observation without reaching true equilibrium (Bolan et al., 1985). The fast reaction between P and Al hydroxide (van Riemsdijk et al., 1975) or iron oxide (Ryden et al., 1977) was concluded to represent adsorption on the surface of the mineral. The slow reaction was hypothesized to be nucleation and growth of a new phase (rate-limiting step) (Chen et al., 1973). Evidence of the growth of an aluminum phosphate phase was given by van Riemsdijk et al. (1975) after 1 day. Nanzyo (1987) determined by diffuse reflectance infrared spectrum that P reacting with noncrystalline aluminum hydroxide and iron hydroxide formed noncrystalline aluminum phosphate, and noncrystalline iron phosphate or binuclear surface complex, respectively. Wavellite [$Al_3(PO_4)_2(OH)_3$ 5H2O] was found to be the stable mineral at low pH (Nriagu, 1976). The rate of phosphate removal was strongly affected by the pH of the system, e.g., the rate increased as pH decreased (Chen et al., 1973). Also, the fast reaction was not affected by solid concentration and temperature, but the slow reaction was affected by them (Chen et al., 1973). Furthermore, P sorption rate was affected by the competition of other specifically sorbed inorganic (sulfate, silicic acid, hydroxyl) and organic (oxalic, citrate) anions for adsorption sites and ionic strength, e.g., low ionic strength increased the activities of phosphate forms. Phosphorus precipitation in the presence of aluminosilicates, aluminum hydrous oxides, and aluminum oxide was investigated by Veith and Sposito (1977). They demonstrated the formation of amorphous Al-phosphate minerals. The formation of the Al-phosphate was favored both by an increase in lability of Al and by decrease in pH (Veith and Sposito, 1977).

Kinetics and equilibrium models have been used to quantify and predict the relation between solution and solid phase concentrations of P in soil-water systems. The most common equilibrium models utilized in soil research are Langmuir and Freundlich equations. Those models explain the experimental data (batch study) satisfactorily in most cases for a given isotherm or solid phase. However, the lack of correlation of model parameters with soil properties most likely results from inaccurate characterization of the adsorption mechanism and poor description of sorption sites (Berkheiser et al., 1980). Kinetic models that apply to rate expressions commonly used in dealing with solution have been used to describe P sorption-desorption by soils (Berkheiser et al., 1980). The effect of time on P sorption by iron and aluminum hydroxide was used by Bolan et al. (1985) to compare six kinetic models-first-order kinetics, second-order kinetics, diffusion equation, a modified Langmuir equation, a modified Freundlich equation, and the Elovich equation. They concluded that these kinetic equations fail to describe the effect of time on sorption partly because the mechanism differs from those postulated and partly because electrostatic effects are not considered when phosphate ions react with a charged surface. They recommended that, to understand mechanisms involved in P sorption, a more complex mechanistic model is required. Electrostatic models have been reviewed by Barrow and Bowden (1987), and Westall and Hohl (1980). However, electrostatic models differ in assumed arrangements of ions near the surface and in specification of the reaction with the surface; most of the parameters used in the models are determined by goodness-of-fit.

### Phosphorus Transport With Water Flow In Acid Sandy Soils

Mathematical models have been used to predict reaction and transport of P applied to soils either as wastewater or as fertilizer. An excellent review of such models was conducted by Mansell and Selim (1981). They divided the models depending upon the theoretical reaction of P with the soil: equilibrium and kinetic dependent, or a combination of both. Selim et al. (1975) utilized a linear reversible equilibrium equation (S=KC) to describe P sorption for the A horizon of a Spodosol. They found that the model did not describe the experimental data. Calculated concentrations of P in the effluent were predominantly higher than experimental results and did not predict excessive tailing observed at large number of pore volumes of the effluent. However, the model accurately described chloride (non-reactive solute) breakthrough curves (BTCs). They related this deficiency in the model to nonlinear sorption or kinetic reaction. Mansell et al. (1977) used a kinetic model with a nonlinear reversible sorption reaction to describe the same A horizon used by Selim et al. (1975). They (Mansell et al., 1977) also observed a deviation between calculated and experimental results, as well as incomplete recovery of applied phosphorus. The left-hand side (adsorption) of the BTC was better described by this model. However, large retardation and extensive tailing could not be described by the model. They suggested that P retention in the A horizon may involve irreversible (precipitation and/or chemical immobilization) as well as reversible (adsorption-desorption) processes. Mansell et al. (1977) added an irreversible sink term (chemical immobilization, $Q=kC$, and precipitation, $Q=kS$) to the model. Although the sink term improved the description of the BTC, neither described the tailing of the right-hand side of the BTC. They concluded that although inclusion of an irreversible sink term improved the ability of the model to describe the effluent data, the rate coefficients were not compatible with batch adsorption isotherm data. Gerritse et al. (1982) also used a convective-diffusive transport model with nonlinear reversible adsorption, and an irreversible sink to describe P movement in undisturbed soil (Spodosol) columns treated with pig slurry. Again, their model did not describe the experimental data, due to factors (pH, Eh, competitive adsorption, effective surface area, etc.) that influence the adsorption isotherm and reaction kinetics.

However, they concluded that mobility of phosphorus added with animal waste can best be described by considering all added P as ortho-P. The most recent work investigating P transport in Spodosols was presented by van der Zee and van Riemsdijk (1986). They utilized P movement using a combination of a fast and reversible adsorption (Langmuir kinetics) and a non-equilibrium, irreversible, precipitation-like process. They concluded that their model gave good agreement between measured and calculated BTCs for the special cases of high feed concentration of P and for the leaching of a column pre-saturated with P. Results from these models have been limited and only successful when applied to conditions in which the soil had relatively low capacity for P sorption. Kanchanasut (1974) investigated the influence of soil water content and flow velocity upon miscible displacement of phosphate in undisturbed cores of a Florida Spodosol. From the kinetic study she found that the fast sorption reaction was completed before one h and that the slow reaction continued beyond 10 h. Analyses of the breakthrough curves indicated that the rates of P movement were in the order of E > A > Bh horizons.

## Objectives of this Research

The main purpose for this dissertation was to investigate the reaction of ortho-P with soil material from Spodosol horizons from selected pasture locations in the watershed north of Lake Okeechobee, as influenced by dairy and beef operations. One objective (Chapter II) was to generally classify the soils and their horizon characteristics. Chapter II presents a soil survey investigation of three different dairies and a beef operation using ground penetrating radar. Information for thickness, depth, and continuity of the three main horizons found in the area Spodosols is presented. The purpose of this chapter was to determine spatial distributions for soil horizons in order to better estimate sampling strategy for these soils. A second objective (Chapter III) was to determine P retention capacity and the actual distribution of phosphorus in soil profiles that have been influenced by dairy operations over long time periods. Three extraction methods were utilized to investigate phosphorus contents in soils from three dairy sites, and P sorption isotherms were used to determine the retention capacities for those soils. Data generated from this work are needed to better describe P transport with water flow through these Spodosols. A third objective (Chapter IV) was to determine the effect of soil-solid mass (i.e., soil-to-solution ratio) and initial P concentration upon P kinetics. Data generated are needed to project P transport during water flow through saturated and unsaturated soil columns as well as under field conditions. A fourth objective (Chapter V) was to investigate the behavior, e.g., sorption and desorption, of phosphorus during water flow through unsaturated/saturated soil columns for three Bh or spodic horizons from soils affected by dairy operations. Results from Chapter V will be used to estimate the retention capacity and the ease of movement of P through soil horizons characteristic of the Lake Okeechobee watershed.

# CHAPTER II
# SOIL SURVEY USING GROUND-PENETRATING RADAR

## Introduction

More than 66% of the soils in Okeechobee County are Spodosols. Spodosols are defined in the Soil Taxonomy (Soil Survey Staff, 1975) as mineral soils that have a spodic horizon with an upper boundary within two meters of the soil surface. One of the more common Great Groups of Spodosols found in Okeechobee County is the Haplaquods. Haplaquods are Spodosols that have developed on nearly level coastal plain in sandy sediments at low elevation. The natural groundwater level is near the soil surface during periods of heavy rain in the summer and occurs at a depth of about 125 cm during the dry spring months. The spodic horizon is principally an accumulation of organic matter and aluminum in the quartz sand matrix (Soil Survey Staff, 1975; Foth and Schafer, 1980). Major mechanisms resulting in the formation of a spodic horizon are (1) the amounts and periods of existence of mobile organic substances, (2) intensity of biological activity, and (3) available amounts of polyvalent cations (especially aluminum and iron) (DeCorninck, 1980).

The spodic horizon (Bh) exhibits different chemical and physical characteristics from overlying horizons within the same soil profile (Calhoun and Carlisle, 1974). With respect to water and solute movement, the important physical characteristics are hydraulic conductivity, water retention, and bulk density. Spodic horizons tend to have greater water retention capacity and bulk density than horizons above it (A and E horizons). The hydraulic conductivity is typically 20 to 30 times smaller than that of the A and E horizons (Hammond et al., 1971; Calhoun and Carlisle, 1974). Lower conductivity tends to result from a greater proportion of micropores (at the expense of macropores) due to accumulation of organic matter and metal oxides on the walls of quartz grains. Also, physical characteristics may vary within each profile. Warrick and Nielsen (1980) grouped soil physical parameters according to relative amounts of variability. At the lower end of variability were bulk density and percent porosity and on the high end were saturated hydraulic conductivity, apparent diffusion coefficient, and pore water velocity.

Spatial variability of soil physical and chemical characteristics is real and continuous and occurs at all levels of resolution (Wilding, 1985). Spatial variability in soils is more commonly expressed as an exponential function of distance and is strongly dependent on the pedogenesis of soils in given environments. Soil survey information can be used in the interpretation of field measured data on spatial variability of soil properties (Wierenga, 1985). Because of the limited number of observations collected during the performance of a soil survey, verification of the mapping units and the soil characteristics represented by these delineations is required (Wilding, 1985). One of the techniques used for mapping verification is Ground Penetrating Radar.

The Ground-Penetrating Radar (GPR) method was described in detail by Shih et al. (1986). The theory of the method has been discussed by Smith (1988). The principle of operation of the GPR technique (Smith, 1988) involves moving an antenna across the soil surface in order to generate a pulse train of electromagnetic radiation in the frequency range of 10-1000 MHz. When the wavetrain encounters a material or boundary of different dielectric properties, partial reflection of the wave occurs. At the layer boundary, the greater the electrical impedance contrast between the two materials, the greater the reflection and transmission of incident electromagnetic energy. The time interval between wave transmission and detection of the reflected wave provides an indicator of the depth to the boundary of soil materials. The GPR was designed specifically to detect interfaces between contrasting layers. Shih et al. (1986) mention that as a general rule, the more abrupt an interface, the stronger the reflected signal and the more apparent are the resulting images on the graph. The GPR provides continuous spatial records of the subsurface soil characteristics, greater aerial coverage per unit sampled than the auger method, and accurate measurement of depth to, and thickness of, several kinds of soil horizons useful for soil survey. The probing depth and resolution of the GPR are, to a large degree, determined by the electrical conductivity of earthen materials (Doolittle, 1987). The principal factors influencing the electrical conductivity of soils are water content, amount and type of salts in solution, and the amount and type of clay (Doolittle, 1987; Johnson et al., 1980). Organic matter may also be a factor (Collins and Doolittle, 1982) influencing electrical conductivity. Doolittle (1987) observed that the GPR does not perform equally well in all soils. He found that the probing depth was reduced from coarse-textured soils to fine-textured soils and by an increase in soluble salts in solution and the proportion of active clays in the soil.

Field experiments have been performed to determine the accuracy and usefulness of the GPR to measure depth to water table and Bh horizon in Spodosols (Collins and Doolittle, 1987; Shih et al., 1986). Both reports demonstrated the efficiency of the GPR. The absolute difference between field data and the values obtained by GPR was within 10 and 6 cm for water table and Bh horizon depths, respectively.

The purpose of this research was to use the GPR method to verify the soil survey (McCollum and Pendleton, 1971) in four areas at three dairies and a beef ranch in Okeechobee County and to determine the spatial continuity of the spodic horizon and the water table. Water flow and solute transport investigations are being conducted by other investigators at these sites through a research project entitled "Biogeochemical behavior and transport of phosphorus in the Lake Okeechobee Basin," funded by the South Florida Water Management District.

## Materials and Methods

Three dairies -- W.F. Rucks, Dry Lake # 1, Larson # 6-- and Williamson Ranch (beef operation) in Okeechobee County were selected for this investigation (Figure 2-1). The latitudinal and longitudinal coordinates for Rucks, Dry Lake, Larson, and Williamson are 27° 27' 32" N and 80° 52' 19'' W, 27° 17' 49" N and 80° 53' 22" W, 27° 15' 42" N and 80° 45' 42" W, and 27° 18' 25" N and 80° 48' 24" W, respectively. The field work was conducted February 3 to 5, 1988. Parallel GPR transects spaced 30.5 m apart were used throughout each area. Evenly spaced reference marks (71 m) were used for horizontal calibration of the GPR output (imprinted on the radar record). The transect length varied from site to site (50 to 300 m). The total number of

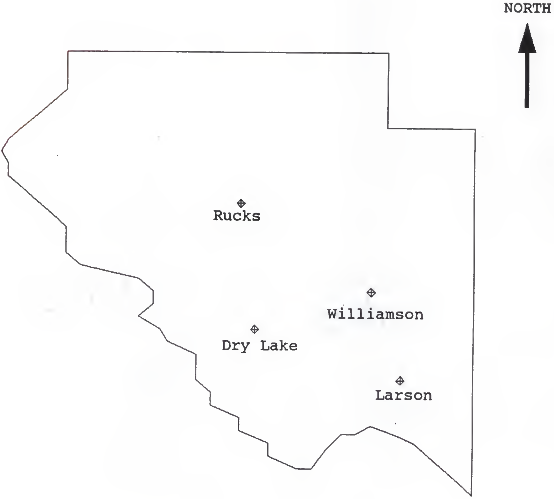


Figure 2-1. General location of the four GPR investigations in Okeechobee County.

transects was 16, 12, 11, and 10 for Rucks, Dry Lake, Larson, and Williamson, respectively.

The W.F. Rucks dairy site is typical of a high quality, improved pasture established on a predominant Myakka soil series (McCollum and Pendleton, 1971). The area selected lies east of the dairy barn and west of a primary ditch feeding into Cypress Slough. The slope throughout the whole site was 0.10% running downslope from west to east. The field area is crossed by three shallow ditches running west-east and 120 m apart. The Dry Lake dairy site is a pasture with Immokalee as the predominant soil series (McCollum and Pendleton, 1971). The northwest edge of the site is bordered by a drainage slough and a shallow ditch (0.6 m deep) forms the southeast site boundary. The general slope of this site is 0.14% running downslope toward the southwest. The predominant soil at the Larson dairy site is a Pomello soil series (McCollum and Pendleton, 1971). The area selected was located southeast of the barn and northwest of Mosquito Creek. The site slope is 0.71% running downslope generally toward the east. The predominant soil at the Williamson ranch site is Immokalee soil series (McCollum and Pendleton, 1971). The site slope is 0.24% running downslope generally toward the north. The Dry Lake and Larson sites had larger animal densities year around than the Rucks and Williamson sites due to the proximity to the respective milking barns.

A 71 by 71 m grid of observation points (auger holes) was constructed at Rucks dairy (calibration site) to provide ground truthing of GPR data for water table and Bh horizon depths. Three to four auger hole measurements were obtained at each site on the transects established for vertical calibration of the GPR data (ground truth). A 30.5 by 71 m grid was used in each of the sites to measure relative surface elevation.

The GPR system used in this research is owned by the United States Department of Agriculture, Soil Conservation Service, at Sebring, Florida. The GPR system was operated by and the data initially interpreted by SCS personnel. The equipment has been previously described in detail by Shih et al. (1986) and Collins et al. (1986). For this study the 120 MHz antenna was used and the scanning time of the GPR was 80 ns. Three to four auger holes were used to calibrate the vertical scale of the GPR graphical output. Shih et al. (1986) determined that three ground-truth profiles are sufficient to scale the radar imagery at a 90% level of statistical accuracy.

Even though the GPR provides continuous data as the antenna is moved across the soil surface at a constant velocity, values to depth of the Bh horizon and water table were selected at 15.2 m intervals in each transect. The total number of points recorded was 240, 276, 203, and 70 for Rucks, Dry Lake, Larson, and Williamson, respectively.

Computer-generated contour maps and surface nets were constructed using the SURFER program from Golden Software, Inc. (Golden, Colorado). The mathematical method used in this program to create the grid was Inverse Distance with a weighting power of 2. The data points within the search area were used in the interpolation of grid elements. The Inverse Distance method is a weighted arithmetic mean, where the weighting factor is the inverse of the distance between neighboring points, squared.

## Results and Discussion

The untouched radar graphic profile shows in most of the transects three contrasting and generally continuous features. These features are the upper soilsurface, an albic (E) and spodic horizon (Bh) interface, and the top of the water table. The strength of the signal (black or gray) depends upon the abruptness of the interface (Shih et al., 1986). Though almost continuous, the image of the spodic horizon was variable (breaks in the continuity) and changes occurred in the tone of gray (from black to light gray). The decrease in the strength of the signal was related to a decrease in the organic carbon content of the spodic horizon and/or a mixing of the spodic horizon with the above layer, in this case the albic horizon (E) (Collins and Doolittle, 1987).

The fundamental difference distinguishing between soil series found at all four sites was the depth to the spodic horizon (Table 2-1). The decreasing order in the depth to the spodic horizon is Putna, Immokalee, Myakka, and Smyrna soils. Each of the points taken from the GPR output graphic was used to determine the depth to the spodic horizon and the soil series. A statistical analysis was conducted to determine the variability of the Bh horizon depth for each site (Table 2-2). The analyses show that the average depth to the spodic horizon increased in the order of Rucks, Dry Lake, Williamson, and Larson. Using average depths to the spodic horizon for each site, the soils could be classified as (Table 2-1) Smyrna, Myakka, Immokalee, and Putna for Rucks, Dry Lake, Williamson, and Larson, respectively. The variability coefficient ranged from 12% to 24%, and Williamson and Larson had the smallest and the largest coefficients, respectively. Detailed investigation of the percentage of points representing the soil series found in each of the sites and in the total research area is presented in Table 2-3. The Dry Lake and Williamson sites had a mixture of Myakka and Immokalee soil series. The Rucks and Larson sites have almost uniform soil, Smyrna and Putna, respectively. This classification differs from that of the soil survey, published in 1971, which did not adequately characterize the soils for the large scale used here. The soils at the Larson site were classified by

Table 2-1. The family name of the soil series and their range in spodic horizon depth (Sawka and Collins, 1986).

| SOIL SERIES | FAMILY NAME | Bh DEPTH RANGE |
|---|---|---|
| SMYRNA | Sandy, Siliceous, Hyperthermic Aeric Haplaquods. | < 50 cm |
| MYAKKA | Sandy, Siliceous, Hyperthermic Aeric Haplaquods. | 50 - 75 cm |
| POMELLO | Sandy, Siliceous, Hyperthermic Arenic Haplahumods | 75 - 125 cm |
| IMMOKALEE | Sandy, Siliceous, Hyperthermic Arenic Haplaquods. | 75 - 125 cm |
| PUTNA | Sandy, Siliceous, Hyperthermic Grossarenic Haplaquods. | 125 - 200 cm |

Table 2-2. Statistical analysis of the variability to depth of the Bh horizon at the four sites.

| | SITE | | | |
|---|---|---|---|---|
| | DRY LAKE | LARSON | RUCKS | WILLIAMSON |
| Number of Points | 276 | 203 | 240 | 70 |
| Depth (cm) | | | | |
| Maximum | 97 | 216 | 66 | 114 |
| Minimum | 38 | 63 | 29 | 63 |
| Average | 71.5 | 150.6 | 45.3 | 83.7 |
| Standard Deviation | 12.92 | 34.89 | 5.62 | 9.90 |
| Variability Coefficient (%) | 18.07 | 23.17 | 12.41 | 11.84 |

Table 2-3. The aerial percentage of soil series found at each site and the approximated total area of each site.

| SITE | SOIL SERIES | | | | APPROX. AREA |
|---|---|---|---|---|---|
| | Smyrna | Myakka | Immokalee | Putna | |
| | % | | | | ($m^2$) |
| RUCKS | 85.7 | 14.3* | 0 | 0 | 105,290 |
| DRY LAKE | 5.1 | 57.2 | 37.7* | 0 | 115,168 |
| LARSON | 0 | 4.4 | 23.2*[a] | 72.4 | 78,858 |
| WILLIAMSON | 0 | 34.3 | 65.7* | 0 | 24,148 |

* Soil classification for entire site according to McCollum and Pendleton, 1971.

[a] Classified as Pomello soil series by McCollum and Pendleton, 1971.

McCollum and Pendleton (1971) as a Pomello soil series (sandy, siliceous, hyperthermic, arenic Haplahumods). The range of depth to the spodic horizon is the same for Pomello and Immokalee soil series and drainage is the difference between these two soils. Both of these soil series can coexist in the same landscape but at different positions. Because Pomello soil series is better drained, it tends to occur higher (elevation) in the landscape than Immokalee soil series. As the only difference between the soil series was depth to the Bh (determined with the GPR), the Great Group (Haplaquods) was assumed constant through the sites. Two-dimensional (topographic map) computer-generated soil series maps were prepared using the data from the GPR graphical output for the Rucks, Dry Lake, Larson, and Williamson sites (Figure 2-2, 2-3, 2-4, and 2-5, respectively). This series of maps gives locations for each soil series and their boundaries. Three-dimensional computer-generated surface net diagrams were also constructed to show the relationship between surface topography and depth to the spodic horizon for each of the sites (Figure 2-6 through 2-9). In general, the change in local elevation (slope) of the spodic horizon is smaller than the change in the local surface topography. However changes are in the same general direction for both depth to the Bh horizon and the surface topography. In other words, the greatest depth to the Bh horizon occurred at the highest

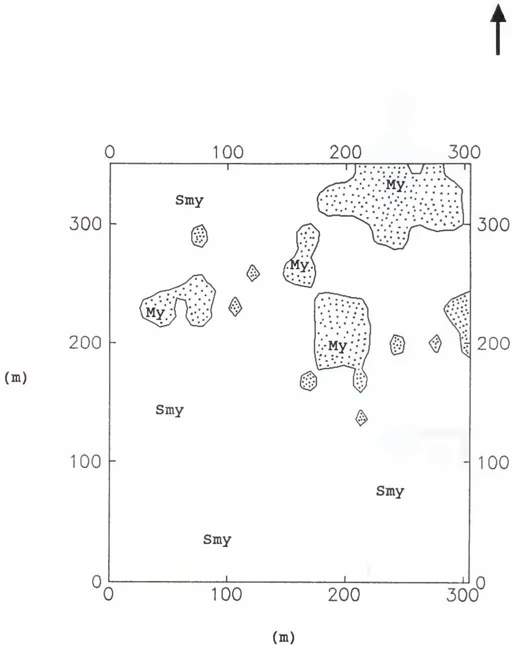


Figure 2-2. Computer generated soil series map for Rucks dairy site. The symbol "SMY" designates Smyrna soil series "MY" designates Myakka soil series.

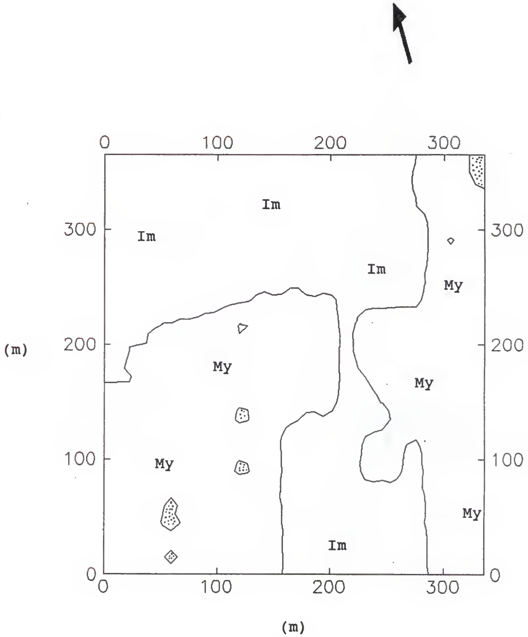


Figure 2-3. Computer generated soil series map for Dry Lake dairy site. The symbol "MY" designates Myakka soil series and "IM" dsignates Immokalee soil series. The shaded areas are Smyrna soil series.

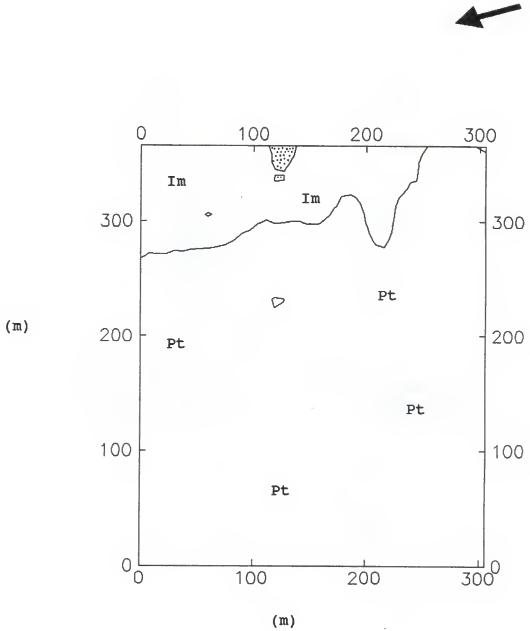


Figure 2-4. Computer-generated soil series map for Larson dairy site. The symbol "IM" designates Immokalee soil series and "PT" designates Putna soil series. The shaded areas are Myakka soil series.

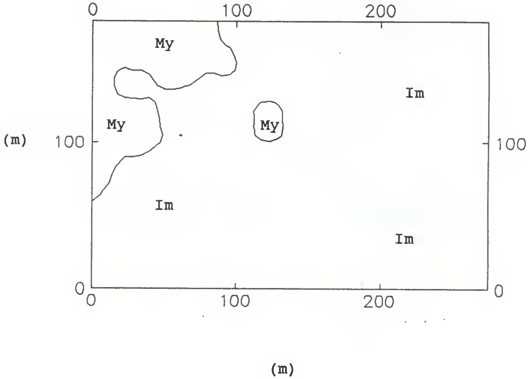


Figure 2-5. Computer-generated soil series map for Williamson dairy site. The symbol "MY" designates Myakka soil series and "IM" designates Immokalee soil series.

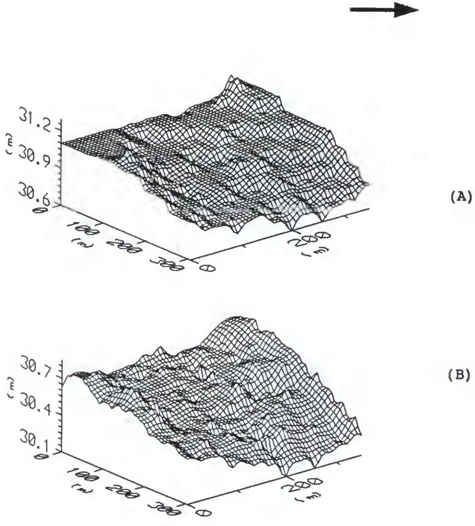


Figure 2-6. Computer-generated surface net diagram for Ruck dairy site. Relative surface elevation is give in (A) and the surface of the spodic is given in (B).

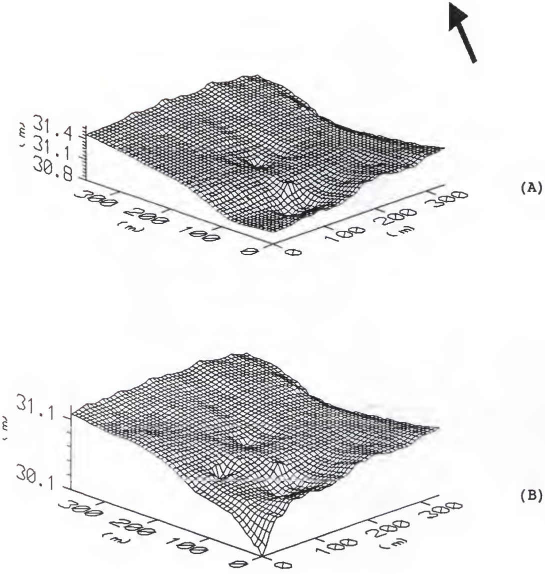


Figure 2-7. Computer-generated surface net diagram for Dry Lake dairy site. Relative surface elevation is give in (A) and the surface of the spodic is given in (B).

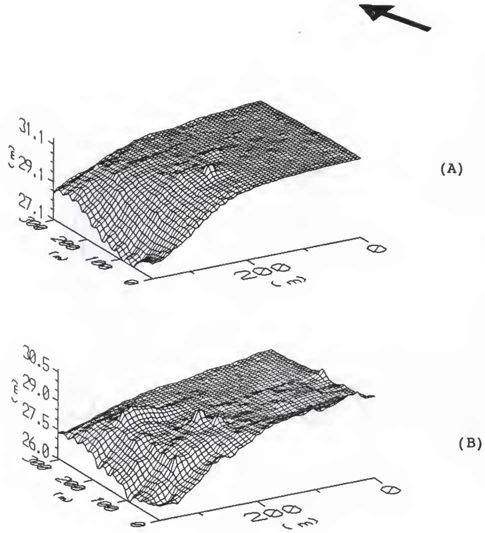


Figure 2-8. Computer-generated surface net diagram for Larson dairy site. Relative surface elevation is give in (A) and the surface of the spodic is given in (B).

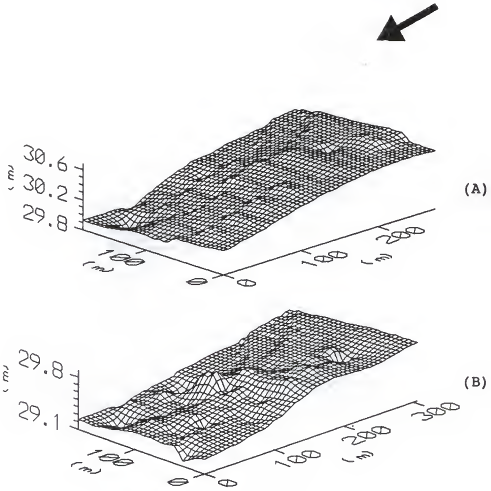


Figure 2-9. Computer-generated surface net diagram for Williamson dairy site. Relative surface elevation is give in (A) and the surface of the spodic is given in (B).

point in the topography. This characteristic behavior was expected and occurred at all sites with the exception of the Rucks dairy.

The Rucks site was dominated (>85%) by Smyrna soil with small pockets of Myakka soils. At the Dry Lake site, the highest point in the topography occurred in association with Immokalee soils (Bh depth >76.2 cm) (Figure 2-7). In general, the surface of the Bh horizon is smoother for the Immokalee than for the Myakka soil series. The Immokalee soil series occurred at the N-NE and S-SW areas. The change in depth to the spodic horizon, from Immokalee to Myakka soil series, was commonly abrupt (0.7% slope). At the Larson site, the highest point was found at the west corner and the soil series associated with it was Putna (Bh depth >127 cm) (Figure 2-8). Generally, both soil series, Immokalee and Putna, show a smooth Bh horizon surface. The transition zone from Immokalee to Putna soil series was less abrupt (or more diffuse) than the topography change. The slope at the 100 m (east side) was 0.7% for the Bh and 2.0% for the soil surface. The Williamson site also had the largest area associated with the deepest Bh horizon. Again, the surface of the Bh horizon at the Immokalee soil series is smoother than the Myakka soil series. At this site, the directions of the slope of the spodic horizon and the soil surface were almost parallel to each other.

The spodic horizon depth generally tended to mimic the local surface topography, but with different local slopes. This change in slope will create different or successive soil series down the landscape. Such a relationship was also described in a Spodosol by Pettry et al. (1965) and Coultas et al. (1979). The relation between different soil series and surface topography is generally known to be due to some combination of microclimate, pedogenesis, and geological surficial processes (Birkeland, 1984). McKeague (1965) related the properties and genesis of Spodosols with their position in the landscape. The shallower spodic horizons tended to have stronger soil development and higher organic matter content than ones located deeper in the profile (Pettry et al., 1965).

The absolute deviation between observed depths (ground truth values) to the spodic horizon at the calibration site (Rucks dairy) and the depths indicated by the scaled radar imagery ranged from 0 to 14 cm; although the absolute deviation for more than 75% of the data points was less than 5 cm. However, three data points, approximately 12% of the data points, had larger deviation compared with the rest of the data (7, 10, and 14 cm). The observed variability was related to the wavy (pockets are wider than their depth) characteristic of the spodic horizon surface. The Bh horizon had a sandy texture, weak structure, and was friable. The thickness of the spodic horizon ranged from 5 to more than 132 cm.

The absolute deviation between observed depths to the water table at the calibration site (Rucks) and depths indicated by the scaled radar ranged from 0 to 40 cm. The output for some of the sites showed a discontinuous water table. The reason for this low accuracy of the GPR could be related to (1) difficulty in differentiating between the spodic horizon and water table signals (shallow water table), (2) the water table is located close to the bottom of the Bh horizon producing a capillary fringe which would make the image of the water table indistinct on the graphic profile (Shih et al., 1986), and (3) decrease in probing depth due to the high electrical conductivity (absorption of electromagnetic pulses) of the Bh horizon (Shih and Doolittle, 1984).

The water table data used to calibrate the GPR output were used to generate a contour map (Figure 2-10). This kind of plot shows isopotential lines and could be used to indicate ground water flow direction. Ground water at Rucks site moved from the NW corner (highest point in the area) to the east side or to the drainage ditch. The elevation of the water table, like the Bh horizon, mimicked the soil surface elevation.

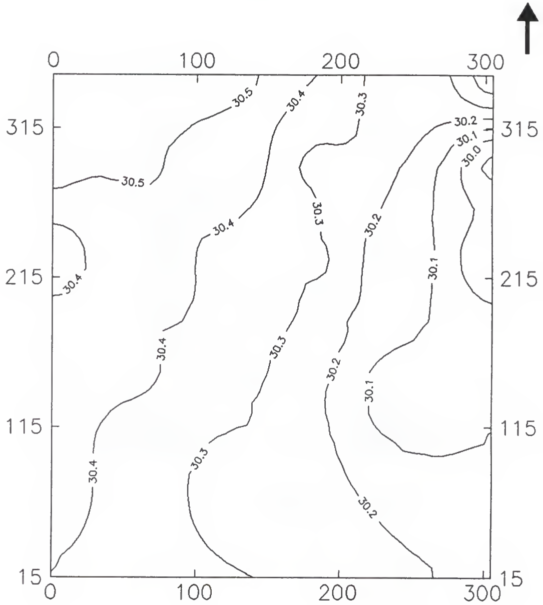


Figure 2-10. Contour map of relative depth to the water table surface at the Rucks dairy site.

## Conclusions

GPR, a fast and relatively accurate method, was used in this research to differentiate between four soil series at four dairy pastures. The depth to the Bh horizon ranged from 30 to 200 cm for all four sites and, in general, the signal was continuous. The data recorded from the graphical output of the GPR were used in the generation of computer graphics. GPR graphical output was used to construct soil series maps and topography and spodic horizon surface diagrams. In general the deepest soil series (Immokalee and Putna) had smoother surfaces than did the shallower Myakka and Smyrna soil series. These plots show that the Bh horizon and the water table imitate the direction but not the slope of the local surface topography. Data presented will be useful in estimating three dimensional water flow and solute transport at the four field sites.

# CHAPTER III
# OBSERVED SPATIAL DISTRIBUTION OF RESIDUAL PHOSPHORUS IN SOIL ALONG TRANSECTS FOR SELECTED DAIRIES IN OKEECHOBEE COUNTY, FLORIDA

## Introduction

Phosphorus sorption (i.e., transfer of P from solution to sorbed phase) in acid soil occurs due to reactions of phosphorus in the solution phase with iron and aluminum hydrous oxides, clay edges, allophane, and other reactive components of the soil. A consensus generally exists that the mechanism of phosphate adsorption by soil minerals involves ligand exchange (Sposito, 1984). Experimental evidence supporting ligand exchange reaction has been presented elsewhere (Mott, 1981; Parfitt, 1978; Hingston, 1981) and extensive investigation studies have been conducted to describe P adsorption on hydrous oxides. The reaction mechanisms for sorption by clay minerals are believed to be similar to those for sorption by iron and aluminum hydroxides (Berkheiser et al., 1980). Muljadi et al. (1966) studied the adsorption of phosphate by kaolinite, gibbsite, and pseudoboehmite and they concluded that the different adsorbents behave in essentially the same manner, and differ only in the number of adsorption sites. Parfitt

(1977) indicated that phosphate reacted with exposed $Al(OH)H_2O$ on kaolinite edges during adsorption experiments. Another important reaction of P in acid soils is precipitation with Al and Fe (Parfitt, 1978; van Riemsdijk et al., 1977). van Riemsdijk et al. (1977), showed that Al-phosphate crystals formed. Parfitt (1978) and Berkheiser et al. (1980) discussed that phosphate could also react with organic acids (humic and fulvic) complexed by aluminum or iron. Thus interaction of organic complexes of metal with sorbed P in the soil could enhance desorption of soil P and enhance P leaching during periods of net water flow. Phosphate adsorption parameters have often been significantly correlated with the aluminum and iron content of the soil (Berkheiser et al., 1980).

The retention and movement of P in Spodosol profiles is related to chemical characteristics for each of the individual horizons (A, E, and Bh). Previous investigations have shown that a large adsorption capacity of the Bh horizon relative to that of the A and E horizons (Bottcher et al., 1986; Selim et al., 1975; Fiskell and Mansell, 1974) greatly limits phosphorus movement (Chaiwanakupt and Robertson, 1976; Selim et al., 1975) through the Bh into the underlying soil. Phosphorus retention in horizons of Spodosols has been correlated with extractable aluminum and iron in the soil (Fiskell and Pritchett, 1979; Ballard and Fiskell, 1974; Yuan, 1966).

Allen et al. (1976,1982) showed that high (greater than 1 mg/L) P concentrations in streams such as Otter Creek, Nubbin Slough, and Mosquito Creek were associated with dairy farming operation in the watershed north of Lake Okeechobee. Some of the P initially fed to dairy cows in feed returns to the soil from cow manure and barn wastewater. These sources of P would be expected to provide a large influence upon the residual phosphorus content of soils (Kuo and Baker, 1982) immediately surrounding the dairies (holding areas) because of higher spatial densities of cows associated with areas near the milking barns. Increasing the amount of residual P generally tends to reduce the sorption capacity of soils (Singh and Jones, 1976) by saturating the soil sorption sites or by reacting with precipitates. The objective of this research was to determine the relative effect of high cow densities in the immediate vicinity of milking operations upon spatial distribution of P for the land contiguous to the barn. Soil samples collected from transects near three milking barns in Okeechobee County were compared for phosphorus extractability and adsorption.

## Materials and Methods

Three dairy pasture sites and one virgin area site were chosen for the transect-sampling study. They were located at Tommy Rucks dairy, McArthur barn # 1 dairy, Larson barn # 5 dairy, and Williamson ranch in Okeechobee County (Figure 3-1). The latitudinal and longitudinal coordinates for Rucks, McArthur, Larson and Williamson are 27°23'14" N and 80°49'58" W, 27°24'00" N and 80°48'40" W, 27°16'18" N and 80°45'55" W, and 27°20'38" N and 80°47'45" W, respectively. The elevation above sea level was approximately 10 m for Rucks, Larson, and Williamson, and 20 m for McArthur. The direction of transects used for Rucks, McArthur and Larson were approximately S 44° E, North, and West, respectively. Soils were sampled between June 8 to 10, 1986 at each of the transect points (i.e., coordinates for soil depth and horizontal distance along the transect) using a well drilling rig (own by Agriculture Engineering Dept.) powered by a gasoline engine to excavate to the sampling depth and a manually operated bucket auger to collect each soil sample. The hole was cased in order to collect soil samples below the existing level of the water table. The field-moist soil samples were stored in a walk-in freezer at 5°C. The transects were located between each milking barn and the closest stream. Distance along transects from the milking barns, the relative elevation of each point in the transects of the three barns, and the water table depth are shown in Table 3-1. The elevation measurements were related to the water level in Otter Creek for Rucks and McArthur transects and to the closest point to Mosquito Creek for the Larson transect. The closest (horizontal distance) stream was Otter

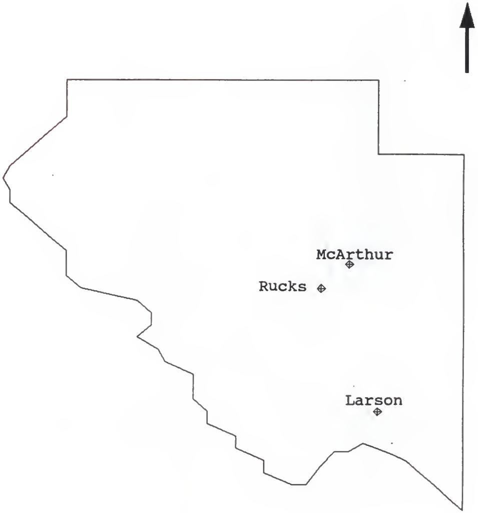


Figure 3-1. General location of the three transects.

Creek for Rucks (520m) and McArthur (830m) and Mosquito Creek for Larson barn (670m). Three randomly chosen sites were sampled at Williamson ranch in a virgin area away from any large creek. Vegetation on the Rucks, McArthur, and Larson transects was improved pasture. The vegetation at the Williamson site was saw-palmetto, pine and flatwoods grasses. Geologically, Rucks, McArthur, and Williamson sites were located on the Penholoway terrace and Larson was located on the Talbot terrace. All the terraces are associated with the Pleistocene geologic age.

Concentrations of water soluble phosphorus (WSP) were determined with duplicate-30 g samples of field moist soil mixed with 30 ml of distilled water in 125 ml plastic bottles. The plastic bottles with the suspensions were tumbled in an end-over-end shaker for 24 hours. After the 24-hour period of tumbling, the suspensions were filtered through Whatman filter paper (No. 42) and analyzed for P. The WSP values were adjusted to the weight of oven-dry soil. Phosphorus content using Mehlich I or "double-acid" phosphorus (MIP) was determined on duplicate 5-g air-dry soil samples, sieved through a 2mm screen, and mixed with 20ml of Mehlich I extracting solution (i.e., 0.05 N HCl + 0.025 N $H_2SO_4$) in 50 ml glass tubes. The suspensions were tumbled for 5 minutes in an end-over-end shaker, filtered through Whatman filter paper (No. 42), and resulting liquid was analyzed for P. Total extractable phosphorus (TEP) was

Table 3-1. Distance from the barn and relative elevation of each site along transects at the Rucks, McArthur, and Larson Dairies.

| | LOCATION | HORIZONTAL DISTANCE (m) | RELATIVE ELEVATION (m) | RELATIVE WATER TABLE ELEVATION (m) |
|---|---|---|---|---|
| RUCKS | | | | |
| | OTTER CREEK | 520 | 0 | 0 |
| | RU1 | 460 | 1.6 | 0.1 |
| | RU2 | 370 | 2.9 | 1.0 |
| | RU3 | 270 | 3.9 | 1.3 |
| | RU4 | 180 | 4.7 | 1.3 |
| | RU5 | 90 | 5.1 | 2.5 |
| | RU6 | 30 | 6.3 | 2.5 |
| | DAIRY BARN | 0 | * | * |
| McARTHUR | | | | |
| | OTTER CREEK | 830 | 0 | 0 |
| | MA1 | 820 | 2.0 | 0.5 |
| | MA2 | 700 | 2.5 | 1.4 |
| | MA3 | 560 | 2.8 | 1.3 |
| | MA4 | 390 | 3.1 | 2.0 |
| | MA5 | 200 | 3.4 | 2.1 |
| | MA6 | 30 | 3.8 | 2.4 |
| | DAIRY BARN | 0 | * | * |
| LARSON | | | | |
| | MOSQUITO CREEK | 670 | * | * |
| | LA1 | 620 | 0 | ** |
| | LA2 | 440 | 0.9 | * |
| | LA3 | 260 | 1.7 | -0.2 |
| | LA4 | 130 | 2.0 | * |
| | LA5 | 20 | 2.4 | 0.5 |
| | DAIRY BARN | 0 | * | * |

* not measured

** water table was not found

determined by the alkaline-oxidation method following the procedure of Dick and Tabatabai (1977). Phosphorus in solution was determined colorimetrically by the ascorbic-acid method (John, 1970). The pH was measured in each sample in solution to soil paste (2:1 ratio) using and Orion Ionalyzer and Orion combination pH electrode (model # 601A and # 8103).

Isotherms for phosphorus adsorption were determined in each of the samples collected. Duplicate 2-g soil samples (air dry and 2mm sieved) were equilibrated in 20 ml of 0.01 M KCl with a range of phosphorus concentrations as $KH_2PO_4$ for 24 hours with 20°C ambient temperature maintained. Initial phosphorus concentrations, $C_o$, were 10, 20, 40, 60, 80, and 100 mg P/l (1 mol/m of P = 30.974 mg/l). The samples were continuously tumbled by an end-over-end shaker. At the end of the 24-hour period, the samples were centrifuged and filtered (Whatman No. 42) and the equilibrium phosphorus concentration ($C_e$) in solution was determined colorimetrically (John, 1970) for each of the initial P concentrations ($C_0$). The initial concentrations of residual phosphorus in the soil, $S_i$, and in the soil solution, $C_i$, were unknown in this experiment. Although, $C_i$ was assumed to be negligible compared with $C_o$ and $C_e$ from the WSP values found in previous experiments, $S_i$ was not necessarily negligible. The amount of phosphorus sorbed (S) was calculated using the difference between the initial and the equilibrium concentrations in solution multiplied by the solution:soil ratio {i.e., $S= 10(C_o-C_e)$}. The Freundlich equation ($S=KC_e^n$) was chosen to fit the adsorption data because it has been used to describe phosphorus adsorption data for several Florida sandy soils (Yuan and Lucas, 1982). Because sorption was not determined for a zero initial concentration ($C_o = 0$) for P in solution during the isotherm experiment, the data were adjusted to maintain mathematical integrity, e.g. when $C=0$ then $S=0$, or $C_e=C_i$ then $S=S_i$. Therefore, the values of S and C, observed at $C_o$ larger than 10 mg P/l, were adjusted with respect to the first set of data points (when $C_o$=10 mg P/l or $S_{10}$ and $C_{10}$) and the initial content of P in the soil ($S_i$). The Freundlich equation was modified to give

$$S - S_{10} = K(C_{e,o}-C_{e,10})^n + S_i \qquad [3\text{-}1]$$

or

$$\blacktriangle S = K(\blacktriangle C)^n \qquad [3\text{-}2]$$

where $\blacktriangle S = S_i+S-S_{10}$ and $\blacktriangle C = C_{e,o}-C_{e,10}$

## Results and Discussion

The transect at each milking barn was located between the barn and the nearest creek in the area. The main differences between locations in a transect were animal density per unit surface area (holding vs pasture) areas, depth to the Bh horizon, and depth to the water table. In general, milking barns were located in higher-elevation, well drained areas. Locations closer to the barn had greater depths to the water table and to the Bh horizon. Holding areas are sites next to the milking barn continuously occupied by cows waiting to be milked. Pasture areas are sites farther from the milking barn and periodically (low frequency) occupied by cows. The ratio of the number of cows per land area as well as the occupation frequency is larger in the holding areas than in the pastures. Horizon designation in the soil profile was performed using color changes and location in the profile. A typical Spodosol profile contains an A horizon (top layer), E horizon (white sand), Bh horizon (organic-dark hardpan) and C horizon (dark, yellowish, light brown subsurface horizon). Precise profile descriptions at each point along the transects were difficult to obtain with the use of the drilling rig. However, the Okeechobee County soil survey (McCollum and Pendleton, 1971) shows that the soil series for the experimental sites were Immokalee and Pomello for Rucks, Myakka for McArthur, Pomello for Larson, and Immokalee for Williamson. The range of depth to the Bh horizon for Myakka soil is between 50 and 76 cm, and for Immokalee and Pomello soils the Bh horizons are deeper than 76 and 102 cm, respectively. Pomello soil series (average water table depth below 1 m) tend to be better drained than the Myakka and Immokalee soil series (average water table depth around 75 cm).

The WSP, MIP, and TEP distributions with depth for each of the points along transects of the Rucks barn are presented in Table 3-2. The sites RU1, RU2, and RU3 were situated within the holding area farthest from the milking barn. High phosphorus concentrations were observed in the top 20 cm for RU1 and RU3 sites. Site RU1 was located next to a fence adjacent to Otter Creek. Also, RU1 was located at the farthest (lowest point) along the transect and 60 m from Otter Creek. RU2 was located in the middle of the holding area. RU3 was located next to a fence and within a zone used as a cow walkway. Holding areas typically do not have a uniform concentration of cows. However, walkways, gateways or doorways, areas under trees, and next to fences within holding areas tend to be used more frequently by cows. The highest MIP and TEP values were found in the top 20 cm sample from RU1. High values of phosphorus at RU1 could be related to occasional overflowing of Otter Creek carrying soluble P, runoff from the areas with higher elevation (Allen, 1988), or a continuous use by cows, e.g. always green pasture on the other side of the fence. Average values plus or minus oneestandard deviations for WSP, MIP, and TEP were 2.3 ± 4.9, 127 ± 332, and 311 ± 807 mg P/kg soil, respectively. Sites RU4, RU5, and RU6 were located within the saameholding area next to the gate to the barn, i.e. an area frequently traveled by cows. RU6 was located in a man-made mound, which is why C horizons were

Table 3-2. Sample depth, horizon designation, pH, and phosphorus extraction data for T. Rucks dairy soil profiles.

| DEPTH | HORIZON | WSP | MIP | TEP* | pH |
|---|---|---|---|---|---|
| (m) | | | ---(mg P/kg soil)--- | | |
| RU1 | | | | | |
| 0.2 | A | 8.0 | 1509 | 3696 | 6.0 |
| 0.8 | Bh | 6.6 | 209 | 228 | 5.7 |
| 1.1 | C | 0.4 | 23 | 68 | 5.2 |
| 1.2 | C | 0 | 13 | 179 | 5.1 |
| 1.8 | C | 0 | 1 | 15 | 5.3 |
| 2.4 | C | 0 | 2 | 16 | 5.2 |
| RU2 | | | | | |
| 0.2 | A | 0.6 | 21 | 16 | 6.4 |
| 0.6 | E | 0 | 0 | 0 | 6.8 |
| 1.0 | Bh | 0 | 21 | 100 | 4.6 |
| 1.2 | Bh | 0 | 65 | 155 | 5.7 |
| 1.8 | C | 0.3 | 9 | 29 | 4.6 |
| 2.4 | C | 0 | 2 | 12 | 5.0 |
| RU3 | | | | | |
| 0.2 | A | 20.2 | 114 | 230 | 6.6 |
| 0.6 | E | 0.2 | 1 | 2 | 7.1 |
| 1.1 | BE | 0.3 | 49 | 67 | 5.8 |
| 1.2 | EB | 0.8 | 153 | 262 | 6.5 |
| 1.8 | BE' | 7.0 | 183 | 392 | 6.2 |
| 2.9 | Bh | 0 | 1 | 80 | 5.2 |
| 4.3 | Bh | 0 | 34 | 359 | 5.5 |
| RU4 | | | | | |
| 0.2 | A | 7.2 | 219 | 621 | 6.8 |
| 0.6 | E | 0.9 | 3 | 7 | 6.5 |
| 1.2 | Bh | 4.2 | 305 | 470 | 6.0 |
| 1.8 | E' | 0.4 | 4 | 12 | 6.4 |
| 2.4 | C | 5.3 | 72 | 90 | 6.6 |
| 3.8 | C | 5.2 | 48 | 444 | 5.5 |
| RU5 | | | | | |
| 0.2 | A | 42.6 | 1539 | 2954 | 6.8 |
| 0.6 | E | 2.8 | 3 | 11 | 6.5 |
| 1.2 | E | 2.2 | 5 | 5 | 6.9 |
| 1.8 | E | 4.1 | 13 | 29 | 7.2 |
| 2.4 | E | 8.6 | 10 | 12 | 7.6 |
| 3.4 | C | 1.2 | 167 | 163 | 7.4 |
| RU6 | | | | | |
| 0.2 | 1C | 16.1 | 68 | 447 | 5.8 |
| 0.6 | 1C | 69.1 | 389 | 510 | 7.9 |
| 1.2 | 2A | 34.2 | 378 | 576 | 8.6 |
| 1.8 | 2E | 1.2 | 7 | 10 | 8.2 |
| 2.4 | 2C | 4.0 | 22 | 34 | 7.9 |
| 3.0 | 2C | 4.5 | 13 | 18 | 7.7 |
| 4.0 | 2C | 5.4 | 46 | 34 | 7.6 |

* WSP, MIP, and TEP are water-soluble, Mehlich-I extractable, and total extractable phosphorus, respectively.

observed to overlay A horizons. The highest values for WSP, MIP, and TEP were found in the top 20 cm for RU4 and RU5 sites. The highest value was found in RU5. The RU6 site had high phosphorus concentrations as deep as 1.2 m or in other words, high P concentrations were found in the old surface and one meter above it. Average plus or minus one standard deviation values for WSP, MIP, and TEP for all depths at RU4, RU5, RU6 were 11.5 ± 17.5, 174 ± 346, and 339 ± 656 mg P/kg soil, respectively. The standard deviation of the average showed, as expected, large variability within the sites and depth. Also, as expected, the amount of extractable P was thus higher in the holding areas closer to the milking barn. The amounts of TEP found in the E or albic horizons sampled were smaller than those from the A and C-Bh horizons sampled. Values of WSP were found deeper in the profile closest to the milking barn. WSP and MIP amounts were equivalent to less than 10% and 50%, respectively, of the TEP amounts.

The WSP, MIP, and TEP distributions with depth along transects at the McArthur site are shown in Table 3-3. MA1 and MA2 were the farthest locations from the milking barn and located in a pasture area between Otter Creek and a drainage ditch. These two points showed the lowest WSP and MIP values for the entire transect. Average values plus or minus one standard deviations for all depths at both sites of WSP, MIP, and TEP were 0.2 ± 0.5, 2 ± 2, and 110 ± 192 mg

Table 3-3. Sample depth, horizon designation, pH, and phosphorus extraction data for McArthur dairy soil profiles.

| DEPTH (m) | HORIZON | WSP | MIP | TEP* | pH |
|---|---|---|---|---|---|
| | | ---(mg P/kg soil)--- | | | |
| MA1 | | | | | |
| 0.2 | A | 0 | 0 | 75 | 4.5 |
| 0.6 | C | 0 | 2 | 56 | 5.2 |
| 1.2 | C | 0 | 2 | 56 | 5.2 |
| 1.8 | C | 0 | 8 | 639 | 5.1 |
| MA2 | | | | | |
| 0.2 | A | 1.7 | 3 | 12 | 5.3 |
| 0.6 | E | 0 | 0 | 0 | 5.3 |
| 1.2 | Bh | 0 | 0 | 3 | 4.0 |
| 1.8 | Bh | 0 | 1 | 8 | 4.2 |
| 2.7 | C | 0 | 2 | 139 | 4.9 |
| MA3 | | | | | |
| 0.2 | A | 6.4 | 14 | 27 | 6.4 |
| 0.6 | Bh | 0.1 | 39 | 131 | 6.6 |
| 1.2 | BE | 0 | 0 | 18 | 5.2 |
| 1.8 | Bh' | 0 | 1 | 232 | 5.2 |
| 2.4 | Bh' | 0 | 2 | 119 | 5.3 |
| MA4 | | | | | |
| 0.2 | A | 2.5 | 10 | 85 | 6.5 |
| 0.3 | C | 0 | 42 | 150 | 5.6 |
| 0.6 | C | 0 | 10 | 47 | 5.8 |
| 1.2 | C | 0 | 0 | 63 | 5.3 |
| 1.8 | C | 0 | 1 | 178 | 5.0 |
| 2.7 | C | 0 | 4 | 156 | 5.1 |
| MA5 | | | | | |
| 0.2 | A | 16.7 | 1104 | 1699 | 6.9 |
| 0.6 | E | 6.4 | 27 | 54 | 7.5 |
| 1.2 | Bh | 14.4 | 50 | 108 | 4.9 |
| 1.8 | C | 0.3 | 3 | 39 | 5.1 |
| 2.7 | C | 0 | 0 | 125 | 5.2 |
| 4.0 | C | 0 | 4 | 282 | 4.9 |
| MA6 | | | | | |
| 0.2 | A | 29.5 | 1157 | 3139 | 6.6 |
| 0.6 | C | 0 | 30 | 276 | 7.1 |
| 1.2 | C | 0 | 23 | 286 | 6.5 |
| 1.8 | C | 0 | 63 | 311 | 7.3 |
| 2.7 | C | 0 | 11 | 270 | 6.8 |

* WSP, MIP, and TEP are water-soluble, Mehlich-I extractable, and total extractable phosphorus, respectively.

P/kg soil. MA3 and MA4 were located in an old tomato field, which had probably been routinely fertilized in the past, and they showed WSP values of 6.4 and 2.5 mg P/kg soil respectively, in the A horizon. Average values plus or minus one standard deviations, from MA3 and MA4, for WSP, MIP, AND TEP were 0.8 ± 1.9, 11 ± 15, and 110 ± 65 mg P/kg soil, respectively. MA5 and MA6 were located closer to the milking barn and in an area that was frequently traveled by cows. The WSP content of the A horizon for MA 5 and 6 were 16.7 and 29.5 mg P/kg soil, respectively; higher than any of the other four transect points. MA5 was the only point that showed some WSP at a depth below 20 cm. The average values for WSP, MIP, and TEP from MA5 and MA6 were 6.1±9.5, 225±428, and 599±916 mg P/kg soil, respectively. Again, higher concentrations for all three forms of extractable P were found closest to the milking barn.

The WSP, MIP, and TEP depth distributions at the Larson transect are shown in Table 3-4. All the locations along the transect at the Larson dairy were located in the same holding area without any particular difference in physiographic and use patterns. The only differences between locations were the distances from the milking barn and Mosquito Creek, and their relative elevations. The highest WSP concentration was found at LA4 (44.5 mg/kg soil), but the largest concentrations of MIP and TEP (1075 and 3575 mg/kg) were found at LA1. Site LA1 was the

Table 3-4. Sample depth, horizon designation, pH and phosphorus extraction data for Larson dairy soil profiles.

| DEPTH (m) | HORIZON | WSP | MIP | TEP* | pH |
|---|---|---|---|---|---|
| | | ---(mg P/kg soil)--- | | | |
| LA1 | | | | | |
| 0.2 | A | 29.1 | 1075 | 3575 | 7.7 |
| 0.6 | Bh | 2.2 | 4 | 8 | 7.6 |
| 1.2 | BC | 7.7 | 8 | 14 | 7.8 |
| 1.8 | C | 12.4 | 28 | 55 | 6.4 |
| 2.7 | C | 14.1 | 32 | 7 | 6.2 |
| LA2 | | | | | |
| 0.2 | A | 3.2 | 33 | 33 | 5.6 |
| 0.6 | E | 3.8 | 6 | 0 | 6.0 |
| 1.2 | Bh | 4.6 | 6 | 3 | 5.1 |
| 2.0 | C | 0.2 | 6 | 4 | 4.7 |
| 2.7 | C | 0.1 | 30 | 52 | 4.3 |
| LA3 | | | | | |
| 0.2 | A | 13.6 | 79 | 253 | 6.1 |
| 0.6 | E | 1.7 | 6 | 18 | 6.5 |
| 1.2 | C | 5.3 | 1 | 11 | 5.9 |
| 1.8 | C | 8.4 | 9 | 21 | 4.2 |
| 2.4 | C | 5.1 | 6 | 13 | 4.3 |
| LA4 | | | | | |
| 0.2 | A | 44.5 | 79 | 1231 | 6.5 |
| 0.6 | E | 7.0 | 23 | 17 | 7.0 |
| 1.2 | E | 6.2 | 18 | 9 | 7.4 |
| 1.8 | C | 9.8 | 22 | 13 | 6.9 |
| 2.4 | C | 7.2 | 15 | 10 | 6.4 |
| LA5 | | | | | |
| 0.2 | A | 7.5 | 25 | 41 | 5.2 |
| 0.6 | E | 9.7 | 64 | 125 | 4.7 |
| 1.2 | E | 2.8 | 67 | 11 | 5.1 |
| 1.8 | C | 0 | 124 | 36 | 4.8 |
| 2.7 | C | 0 | 57 | 29 | 4.3 |

* WSP, MIP, and TEP are water-soluble, Mehlich-I extractable, and total extractable phosphorus, respectively.

farthest from the milking barn or the closest to Mosquito Creek and the fence. Also, LA1 was located down slope from the barn and the water table and Bh horizon were closer to the surface. These factors will favor runoff during heavy rains. Values of WSP were found for all the sampled depths,with higher concentrations in the top 20 cm. The average values plus or minus one standard deviations for WSP, MIP, and TEP at all depths and sites were 6.1 ± 9.6, 73 ± 207, and 224 ± 725 mg P/kg soil, respectively.

All samples collected were used to evaluate linear correlations between the three forms of extractable phosphorus. No linear relations were found between MIP or TEP and WSP. However, MIP and TEP values were linearly related (TEP = 86 + 33.2MIP, $r^2 = 88\%$). Some of the values of P extracted with MIP were larger than the TEP values. This was related, first, to the similarity in the amount of extracted P for both methods and to the error caused by the use of different solution:soil ratios in the extraction procedures for TEP (120 mg/l) compared with the procedure for MIP (4 mg/l). The analytical error, constant for both P analyses, will be multiplied by the solution:soil ratio causing larger errors to TEP values than MIP.

In addition to transects taken at the three dairy sites, samples were collected in a virgin soil (not affected by cultivation or pasturing) with native vegetation at Williamson Ranch. Three profiles were sampled and analyzed

(Table 3-5) for comparison with the holding and pasture areas (Rucks, McArthur, and Larson). Average values plus or minus one standard deviations for all depths and sites were 0.4 ± 0.6, 6 ± 13, and 50 ± 77 mg P/kg soil for WSP, MIP, and TEP, respectively. The WSP content of the A horizon (top 20cm) of the virgin soil was approximately 1 mg/kg soil. The WSP content below 20 cm was virtually zero. The values of MIP were the same as WSP, i.e. all the MIP was water soluble. The average TEP values for all soils sampled was 50 mg/kg soil, and the highest values were less than 300 mg/kg soil, found at depths below 1.5 m. In general, the TEP content increased with depth and the amount of WSP decreased with depth. These results probably indicate that the more stable form of P (TEP), better crystallized and less mobile, is found deeper in the profile, compared with the less stable form of P (MIP). No trend was found for MIP values. The WSP, MIP, and TEP values measured in soil at the holding and pasture areas from the three dairy sites were higher than those for the native site. In 15 out of the 17 sites sampled, the top 20 cm had a WSP value higher than 1 mg P/kg soil. Twenty five percent of the soil samples had higher values of TEP than the highest value of TEP in the native soil. The highest concentrations of MIP and TEP were found in the top 20 cm and the concentrations ranged between 10 and 200 times larger than those found in virgin soils. Comparing the values of WSP,

Table 3-5. Sample depth, horizon designation, pH, and phosphorus extraction data for three native soil profiles at Williamson.

| DEPTH (m) | HORIZON | WSP | MIP | TEP* | pH |
|---|---|---|---|---|---|
| | | ---(mg P/kg soil)--- | | | |
| WI1 | | | | | |
| 0.1 | A | 2.0 | 0 | 11 | 5.2 |
| 0.2 | A | 1.5 | 0 | 5 | 5.1 |
| 0.6 | Bh | 0 | 0 | 32 | 4.2 |
| 1.2 | C | 0 | 14 | 39 | 4.1 |
| WI2 | | | | | |
| 0.2 | A | 0.7 | 0 | 6 | 5.1 |
| 0.9 | E | 0.1 | 0 | 0 | 5.6 |
| 1.5 | C | 0.1 | 50 | 160 | 4.1 |
| 2.7 | C | 0 | 2 | 11 | 4.3 |
| WI3 | | | | | |
| 0.2 | A | 0.1 | 1 | 7 | 5.0 |
| 0.3 | C | 0.1 | 0 | 0 | 5.6 |
| 0.6 | C | 0 | 0 | 10 | 4.7 |
| 1.5 | C | 0 | 10 | 110 | 4.3 |
| 2.7 | C | 0 | 1 | 263 | 4.5 |

* WSP, MIP, and TEP are water-soluble, Mehlich-I extractable, and total extractable phosphorus, respectively.

MIP, and TEP between soil located near the dairy barns with native soil showed the effect of animal manure, e.g. increases in all three forms of extracted phosphorus occurred for the soil adjacent to the barns. However, high P contents away from the milking barn were found at LA1, MA1 and RU1 transect locations. These three locations were characterized by a shallow water table level closer to the surface and were located on the lowest relative elevation in each transect. With these characteristics, they are susceptible to being affected by flooding from the nearby creek and runoff from upslope areas (Allen, 1988). P data collected next to all of the barns were relatively consistent values of approximately 9, 150, and 400 mg P/kg soil for WSP, MIP, and TEP. These results indicated that the WSP accounts only for a small percent (2%) of the total P in the soil. However, P extracted by Mehlich I is considered to be available to plants or relatively available for movement with the water and accounted for more than 30% of the total P. Still, those values are at least 10 times higher than the ones found for the native soils. The transect data did not show details about the P transport (pathway) from the milking barn to the creek. The reason for this was that the sampling procedure (transect) assumed uniform distribution of P in each area, which was not the case in this investigation where the animal density varied within each area (anisotropic condition). The pH for the native soil (Williamson) ranged for the A and E horizons from 5.0 to 5.6 and for the Bh and C horizons from 4.1 to 4.7. For all three dairies, high pH, higher than the ones at the natives (pH>6) for all depths, was associated with high extractable P. Those high pH values were detected in all the depths and could be related to the manure and wastewater. The pH values above 8 (RU6) could be related to high soil sodium content (Bohn et al., 1979) due to the use of water from high-salt wells (Allen et al., 1976).

An initial concentration of 10 mg/l (smallest P concentration in solution used in this research and chosen randomly) of phosphorus in aqueous solution was utilized to characterize the adsorption or desorption capabilities for stirred suspensions of each of the soils sampled. The equilibrium concentration values were also used to correct the P adsorption values used to fit the modified [Eq. 3-1] Freundlich equation ($C_{e,10}$). Those values are presented in Table 3-6 for all the three dairies and the native soil. The soil sampled could be placed in three distinct groups: soils sampled that desorbed P ($C_{e,10}$ > 10 mg/l); soils sampled where the initial P concentration did not change ($C_{e,10}$ = 10 mg/l); and, soils that adsorbed P ($C_{e,10}$ < 10mg/l). The soils that desorbed or did not change the initial P concentration (marked * on Table 3-6) did not change their behavior for P concentrations above 10 mg P/l and their values were not fitted to the modified Freundlich isotherm

Table 3-6. Equilibrium concentration ($C_{e,10}$) after 10 mg/l of P in aqueous solution was applied to the soil sampled from each point along transects at Rucks, McArthur, Larson, and Williamson sites.

| DEPTH (m) | $C_{e,10}$ (mg P/l) |
|---|---|
| RU1 | |
| 0.2 | 12.9* |
| 0.8 | 9.5 |
| 1.1 | 1.5 |
| 1.2 | 0.1 |
| 1.8 | 0.9 |
| 2.4 | 0.1 |
| RU2 | |
| 0.2 | 9.5* |
| 0.6 | 10.0* |
| 1.0 | 0.7 |
| 1.2 | 2.4 |
| 1.8 | 1.4 |
| 2.4 | 1.2 |
| RU3 | |
| 0.2 | 12.1* |
| 0.6 | 9.7* |
| 1.1 | 8.6* |
| 1.2 | 6.8 |
| 1.8 | 11.4* |
| 2.4 | 0.4 |
| 4.3 | 0.2 |
| RU4 | |
| 0.2 | 11.3* |
| 0.6 | 10.5* |
| 1.2 | 8.7 |
| 1.8 | 10.2* |
| 2.4 | 11.4* |
| 3.8 | 0.2 |
| RU5 | |
| 0.2 | 36.9* |
| 0.6 | 10.5* |
| 1.2 | 10.6* |
| 1.8 | 10.7* |
| 2.4 | 11.1* |
| 3.4 | 13.5* |
| RU6 | |
| 0.2 | 1.4 |
| 0.6 | 31.6* |
| 1.2 | 22.7* |
| 1.8 | 10.6* |
| 2.4 | 10.5* |
| 3.0 | 10.5* |
| 4.0 | 10.1* |
| MA1 | |
| 0.2 | 0.2 |
| 0.6 | 0.1 |
| 1.2 | 0.1 |
| 1.8 | 0.0 |
| MA2 | |
| 0.2 | 10.3* |
| 0.6 | 10.0* |
| 1.2 | 6.9 |
| 1.8 | 0.4 |
| 2.7 | 0.1 |
| MA3 | |
| 0.2 | 10.9* |
| 0.6 | 1.5 |
| 1.2 | 0.3 |
| 1.8 | 0.0 |
| 2.7 | 0.0 |
| MA4 | |
| 0.2 | 10.5* |
| 0.3 | 0.4 |
| 0.6 | 2.8 |
| 1.2 | 0.0 |
| 1.8 | 0.0 |
| 2.7 | 0.0 |
| MA5 | |
| 0.2 | 26.6* |
| 0.6 | 11.5* |
| 1.2 | 9.5* |
| 1.8 | 1.3 |
| 2.7 | 0.0 |
| 4.0 | 0.2 |
| MA6 | |
| 0.2 | 28.6* |
| 0.6 | 1.0 |
| 1.2 | 0.5 |
| 1.8 | 2.6 |
| 2.7 | 0.6 |
| LA1 | |
| 0.2 | 12.2* |
| 0.6 | 7.0 |
| 1.2 | 2.8 |
| 1.8 | 0.1 |
| 2.7 | 0.1 |
| LA2 | |
| 0.2 | 10.2* |
| 0.6 | 10.7* |
| 1.2 | 10.8* |
| 2.0 | 6.6 |
| 2.7 | 2.9 |
| LA3 | |
| 0.2 | 13.1* |
| 0.6 | 10.1* |
| 1.2 | 10.0* |
| 1.8 | 9.8* |
| 2.4 | 10.0* |
| LA4 | |
| 0.2 | 27.2* |
| 0.6 | 12.5* |
| 1.2 | 11.9* |
| 1.8 | 12.0* |
| 2.4 | 11.3* |
| LA5 | |
| 0.2 | 22.1* |
| 0.6 | 10.6* |
| 1.2 | 11.0* |
| 1.8 | 11.2* |
| 2.7 | 10.8* |
| WI1 | |
| 0.1 | 9.8* |
| 0.2 | 9.8* |
| 0.6 | 0.4 |
| 1.2 | 0.3 |
| WI2 | |
| 0.2 | 9.7* |
| 0.9 | 9.9* |
| 1.5 | 1.1 |
| 2.7 | 4.1 |
| WI3 | |
| 0.2 | 9.9* |
| 0.3 | 10.0* |
| 0.6 | 2.5 |
| 1.5 | 0.0 |
| 2.7 | 0.7 |

*isotherm data not fitted to the modified Freundlich equation.

[Eq. 3-1]. The $C_{e,10}$ values were representative of the sorption (desorption or adsorption) behavior of each of the samples and could be used to characterize the sorption capacity of other soils.

The modified Freundlich adsorption isotherm equation [1] was fitted to the adsorption data. The coefficients K, n, and the correlation coefficient are shown in Table 3-7 for Rucks, McArthur, Larson, and Williamson transects. Sampled soil that desorbed or did not adsorb phosphorus (approximately 50% of the number of soils sampled) upon addition of P-laden aqueous solution were not included in the curve fitting (see Table 3-6). Those soils had either a small adsorption capacity ($C_{e,10}$ > 10 mg/l) or a high WSP value. Almost all of the A and E horizons, with or without WSP, did not sorb phosphorus. The average correlation coefficient for all the fitted equations was 89%. However, 69% of the fitted equations have a correlation coefficient equal to or larger than 95%. Correlation coefficients larger than 76% are significant to the 0.1% level, which indicates that the fitted equation adequately represents the data. The average n value was 0.395 with a standard deviation of 0.014. Large values of n found at RU1, MA2, MA6, and LA1 locations could only be related to variability in the data. However, these high values did not greatly influence the average value of n. Values for K were highly variable and ranged from 3.7 to 396.8 l/kg soil. The values of K were correlated with values for WSP, MIP, and TEP. However, no significant linear or logarithmic relationships were found between them. Most of the soils that did not sorb P had pH values above the native sites. Sorption isotherm studies were also carried out on the native soils sampled (Table 3-7). The soil samples collected in the top 30 cm did not adsorb or desorb phosphorus when placed in contact with aqueous phosphorus solution. The equation fitted to the samples that sorbed phosphorus had n values (0.388 ± 0.104) almost the same as the ones from the holding and pasture areas. Other authors showed similar mineral values for kaolinite (Low and Black, 1950) and soils (Yuan and Lucas, 1982; de Camargo et al., 1979). High n values were found at site 2, which had a low (46%) correlation coefficient, e.g., the fitted equation did not represent the data. The values of K were also variable and ranged from 2.7 to 152 l/kg soil.

The sorption buffering capacity (B(C)) is defined here as the slope of S versus C plot (Mansell and Selim, 1981). For a nonlinear equation, as the Freundlich, the buffering capacity ($\blacktriangle S/\blacktriangle C$) is usually expressed as $B(C_e)=nKC_e^{n-1}$. However the modified sorption buffering capacity as used here is given as $B(\blacktriangle C)=nK(\blacktriangle C)^{n-1}$ where $\blacktriangle S=S_i+S-S_{10}$ and $\blacktriangle C=C_{e,o}-C_{e,10}$. Sorption buffering capacity was calculated with $C_{e,10}$ and the values are presented in Table 3-7. The buffering capacity predicted by the Freundlich equation tends to increase with a decrease in the equilibrium P concentration in solution (Mansell and Selim, 1981), an increase of K, and increased n values. Phosphorus movement will be restricted with increasing values for the buffer capacity. The buffer capacity for all of the dairy soils used here ranged from 0.9 to 11226 l/kg soil. The values of buffer capacity for the native soils were also variable and ranged from 1 to 433 l/kg soil. The surface horizon from the holding areas did not sorb any phosphorus, nor did the top horizon (A horizon) from the native soil sampled. Albeit, the measured WIP and TEP contents of field soil from the holding areas were a lot higher than those from the native areas. WSP, MIP, and TEP did not affect the ability of the subsurface horizon to sorb (sorption buffer capacity) phosphorus. The higher sorption buffer capacities of the Bh and C horizons for similar Spodosols (Fiskell and Mansell, 1974; Selim et al., 1975) have previously been shown to be related to the high Al, Fe, and organic matter content in the soil. When the equilibrium concentration was less than 1 mg P/l, sixty four percent of the Bh and C horizons fitted to the Freundlich equation adsorbed more than 90% of the P in solution. The soils for which the values of $C_{e,10}$ in solution P were larger than 10 mg P/l, desorbed more WSP and less MIP. This was caused by the change in soil:solution ratio, from 1:1 to

Table 3-7. Phosphorus adsorption isotherm parameters and correlation coefficients for soil samples from Rucks (RU), McArthur (MA), Larson (LA), and Williamson (WI) sites.

| SITE | SAMPLE DEPTH (m) | ISOTHERM COEFFICIENTS K (l/kg) | n | BUFFER CAPACITY (l/kg) | CORRELATION COEFFICIENT $r^2$ (%) |
|---|---|---|---|---|---|
| RU1 | | | | | |
| | 0.8 | 6.44 | 0.606 | 1.60 | 88.4 |
| | 1.1 | 19.07 | 0.468 | 7.30 | 69.0 |
| | 1.2 | 121.29 | 0.489 | 274.12 | 95.5 |
| | 1.8 | 33.78 | 0.381 | 13.37 | 97.5 |
| | 2.4 | 95.49 | 0.295 | 142.82 | 94.1 |
| RU2 | | | | | |
| | 1.0 | 71.37 | 0.440 | 37.46 | 98.0 |
| | 1.2 | 30.37 | 0.440 | 8.16 | 93.0 |
| | 1.8 | 25.22 | 0.402 | 8.33 | 95.6 |
| | 2.4 | 43.10 | 0.304 | 11.41 | 91.9 |
| RU3 | | | | | |
| | 1.2 | 7.07 | 0.394 | 0.87 | 44.1 |
| | 2.9 | 124.61 | 0.409 | 82.80 | 94.5 |
| | 4.3 | 139.05 | 0.427 | 158.61 | 75.2 |
| RU4 | | | | | |
| | 1.2 | 7.90 | 0.494 | 1.31 | 65.6 |
| | 3.8 | 107.07 | 0.426 | 114.81 | 98.4 |
| RU6 | | | | | |
| | 0.2 | 40.74 | 0.434 | 14.68 | 96.0 |
| MA1 | | | | | |
| | 0.2 | 128.60 | 0.350 | 113.80 | 99.2 |
| | 0.6 | 75.96 | 0.276 | 97.31 | 97.8 |
| | 1.2 | 101.46 | 0.278 | 245.29 | 97.0 |
| | 1.8 | 300.43 | 0.316 | 858.28 | 95.9 |
| MA2 | | | | | |
| | 1.2 | 3.78 | 0.552 | 0.88 | 34.3 |
| | 1.8 | 97.35 | 0.331 | 65.04 | 94.5 |
| | 2.7 | 258.56 | 0.358 | 633.44 | 98.8 |
| MA3 | | | | | |
| | 0.6 | 43.41 | 0.382 | 13.24 | 98.3 |
| | 1.2 | 48.05 | 0.342 | 37.98 | 97.9 |
| | 1.8 | 396.75 | 0.310 | 2950.40 | 99.4 |
| | 2.4 | 283.05 | 0.286 | 11226.14 | 99.8 |

Table 3-7. Continued.

| SITE | SAMPLE DEPTH | ISOTHERM COEFFICIENTS |  | BUFFER CAPACITY | CORRELATION COEFFICIENT |
|---|---|---|---|---|---|
|  |  | K | n |  | $r^2$ |
|  | (m) | (l/kg) |  | (l/kg) | (%) |
| MA4 |  |  |  |  |  |
|  | 0.3 | 158.37 | 0.371 | 98.47 | 98.5 |
|  | 0.6 | 9.51 | 0.473 | 2.64 | 78.9 |
|  | 1.2 | 124.33 | 0.311 | 572.72 | 99.3 |
|  | 1.8 | 215.46 | 0.322 | 1574.78 | 98.9 |
|  | 2.7 | 119.08 | 0.309 | 886.71 | 99.5 |
| MA5 |  |  |  |  |  |
|  | 1.8 | 29.14 | 0.405 | 9.92 | 95.4 |
|  | 2.7 | 99.75 | 0.384 | 2699.23 | 98.9 |
|  | 4.0 | 86.56 | 0.392 | 80.81 | 99.1 |
| MA6 |  |  |  |  |  |
|  | 0.6 | 80.52 | 0.483 | 39.94 | 91.0 |
|  | 1.2 | 144.71 | 0.497 | 99.93 | 95.6 |
|  | 1.8 | 51.50 | 0.477 | 14.81 | 98.0 |
|  | 2.7 | 195.81 | 0.604 | 144.78 | 96.9 |
| LA1 |  |  |  |  |  |
|  | 0.6 | 12.12 | 0.608 | 0.04 | 92.3 |
|  | 1.2 | 21.07 | 0.574 | 3.71 | 95.8 |
|  | 1.8 | 278.14 | 0.380 | 3.43 | 94.3 |
|  | 2.7 | 90.57 | 0.305 | 7.82 | 95.1 |
| LA2 |  |  |  |  |  |
|  | 2.0 | 10.65 | 0.022 | 393.50 | 5.0 |
|  | 2.7 | 17.19 | 0.407 | 159.83 | 84.8 |
| WI1 |  |  |  |  |  |
|  | 0.6 | 74.29 | 0.316 | 44.70 | 98.5 |
|  | 1.2 | 62.48 | 0.353 | 45.19 | 97.5 |
| WI2 |  |  |  |  |  |
|  | 1.5 | 48.41 | 0.386 | 18.13 | 97.6 |
|  | 2.7 | 2.69 | 0.629 | 1.00 | 46.6 |
| WI3 |  |  |  |  |  |
|  | 0.6 | 18.50 | 0.345 | 3.47 | 75.5 |
|  | 1.5 | 151.95 | 0.289 | 433.05 | 98.7 |
|  | 2.7 | 43.35 | 0.398 | 22.36 | 99.0 |

1:10 (Berkheiser et al., 1980), and the high solubility or exchangeability of the P form in the soil.

The A and E horizons from the dairy and native sites showed no measurable P sorption capacity under the experimental conditions of this research. However, A and E horizons of locations next to the dairy barns (and next to the creeks) showed high P concentrations. These indicate that different environmental (physical and chemical) conditions exist between the soils (A and E horizon) next to the barn and the pasture/native soils. Larger accumulations of cow manure and urine (i.e., organic matter, cations, and anions) were found next to the barn. One of the characteristic reactions that relates to P accumulation is precipitation. Bottcher et al. (1986) showed that high concentrations of MIP were related to Mehlich I extractable calcium (Ca) in the surface horizons in similar dairy holding areas (Okeechobee). The neutral to slightly alkaline pH values observed in the surface horizon possibly indicate a form of calcium phosphate precipitation. Mehlich I extractable calcium ranged from 28 to 130 g/kg soil in the top 10 cm and those values were related to phosphorus concentration of 5 to 41 g/kg soil. High concentrations of Mehlich I extractable aluminum (Al) were found in subsurface horizons (Bh and C horizons). Mehlich I extractable potassium and iron accumulated on the surface and subsurface horizons, respectively, but their concentrations were lower than Ca and Al concentrations (Bottcher, et al., 1986). High concentrations of P and Ca or Al possibly will indicate that P is being precipitated in the surface (A) and subsurface horizons (Bh and C). Flaig et al. (1986) stated that application of secondary municipal wastewater to sandy soil enhanced P retention in the soil due to the presence of cations and organic material simultaneously with the wastewater. Complexation between P and other chemical components of the manure will enhance P accumulation.

## Conclusions

Density of cows per unit of land area was observed to influence the phosphorus status of soil in the land adjacent to the dairy barns. As expected, soil sampled closest to the barns of three dairies examined in a region north of Lake Okeechobee in South Florida showed higher contents of water soluble phosphorus (WSP), Mehlich I extractable phosphorus (MIP), and total extractable phosphorus (TEP) values in the surface soil horizon (A or newly deposited soil) and they occurred deeper in the profile. Also, high P concentrations were found next to the creek in the A horizon and in the deeper horizons. The high concentrations near the creek possibly relates to the hydrologic cycle of the creek and its the effect on the chemistry of the adjacent soil (reduced conditions), and the accumulation in the creek water-solution of other ions. Also, the soil horizons from areas next to the creek are affected more by upstream influxes of P from other dairies. No good explanation for these phenomena could be drawn from the data presented here. The different extractable forms of P did not indicate a pathway for P movement from the barn to the creek (decrease in P concentration with increase in distance away from milking barn). However, due to the low or negligible buffer capacity of the A and E horizons, these results are understandable. Organic and inorganic chemical components of the manure and wastewater may have enhanced P retention in these horizons. Each sample collected represented only one point in the landscape, and, due to the localized "application of the manure" by the cows, high variability in the data was discovered. A larger number of samples or wider sampling transects will be useful for future work and for a better understanding of the P pathway (milking barn to creek).

The capability of the soil to accumulate or sorb phosphorus was characterized by sorption buffer capacity calculated from a modified Freundlich adsorption equation. The A and E horizons did not show a finite value of buffer capacity for phosphorus sorption. If the values of WSP were higher than zero, both horizons desorbed phosphorus when in contact with a P-laden aqueous solution. The Bh and C horizons showed variable buffering capacities. The buffer capacities of these two horizons were influenced by the K and the $C_e$ values and were not related to the extractable P. Precipitation possibly occurred during the accumulation of P in the locations next to the milking barns with soils having essentially no buffering capacity.

# CHAPTER IV

# PHOSPHORUS SORPTION BY A Bh HORIZON FROM A HAPLAQUOD: EFFECT OF TIME, INITIAL CONCENTRATION, AND SOIL SOLIDS CONCENTRATION IN AQUEOUS SOIL SUSPENSION

## Introduction

A batch technique (i.e. stirred aqueous soil suspension) is commonly used to investigate ortho-P sorption-desorption by soils. Some of the disadvantages of this technique include difficulties in: 1) evaluating rapid reactions, i.e. ion exchange (Sparks, 1985); 2) properly measuring the kinetics of a chemical reaction (i.e. the technique must not change the reactant concentration in solution) (Zasoski and Burau, 1978); 3) optimizing the mixing of solution and soil without particle breakdown (Barrow, 1983). However, advantages for using the batch technique are that soil and solution are easily separated, there is a large volume of solution for analysis (Barrow, 1983), and it can easily be incorporated as a routine lab technique without extra equipment.

Soil scientists generally agree (see Chapter 1) that the overall reaction of P with soil materials consists of a relatively fast reaction followed by one with a relatively slow reaction rate. These two reactions may operate in parallel or in series (successive). The slow sorption of P reaction continues without reaching a true chemical equilibrium (Bolan et al., 1985) even over periods of months or years. Soil components that have been observed to show this behavior include gibbsite (Chen et al., 1973; Kuo and Lotse, 1973; Haseman et al., 1950), goethite (Yekini et al., 1985; Haseman et al., 1950), hematite (Kuo and Lotse, 1973), kaolinite (Chen et al., 1973, Haseman et al., 1950), amorphous aluminum hydroxide (van Riemsdijk et al., 1975; Hsu and Rennie, 1961), and allophanic material (Imai et al., 1981). A P kinetic study of a Bh horizon (Kanchanasut, 1974) showed a fast (less than a hour) and a slow reaction (continuing after 10 hours). Phosphorus reaction with soil is affected by various factors operating simultaneously. Some of these factors are solution pH (Chen et al., 1973), electrolyte concentration (Bar-Yosef et al., 1988), P concentration in solution, soil solids concentration (Chen et al., 1973), and previous P addition (Berkheiser et al., 1980). The objectives of this experiment were to determine the effect of contact time, initial P concentration, and soil solids concentration in a stirred aqueous suspension of soil upon the resulting P concentration in solution, pH, and calcium and aluminum released from a Bh horizon taken from South Florida.

## Materials and Methods

Soil samples were collected from a Spodosol under beef production during the summer of 1987 at Williamson Ranch (see Chapter II) in Okeechobee County in South Florida. The soil series for the soil at that site was Myakka (sandy, siliceous, hyperthermic Aeric Haplaquod). The Bh horizon was located at 53-cm depth and was 20-cm thick. The soil was air dried and sieved through a 2-mm screen before being used.

Duplicate soil samples were equilibrated in 25-ml P-laden aqueous solution of 0.01 M KCl. The effect of soil-to-solution ratio or concentration of soil solids on P sorption was investigated by adjusting soil mass using 12.5, 6.25, 4.17, 3.13 and 2.5 g per 25 ml of aqueous suspension of soil, and keeping the volume of solution constant (solution:soil ratio of 2, 4, 6, 8, and 10 ml/g). The values for solution-to-soil ratio under field conditions are commonly below approximately 0.3 ml/g under conditions of water saturation. Contact times used were 0.5, 1,5, 24 (1 day), 168 (1 week), and 2016 (3 month) h. Short (0.5 h) and long times (2016 h) were utilized to study the fast and slow reactions. The 0.5-h time period was the shortest time for solution and soil separation. The initial concentrations of P in solution ($C_0$) used were 10.1, 20.3, 40.2, 62.3, 79.8, and 101.8 mg P/l as $KH_2PO_4$. The absence of a $C_0$ with zero-P was based on the results reported in Chapter III where most of the Bh horizon soil sampled did not desorb P (WSP=0 or below detection limit), and on the main objective of this chapter which was to investigate the P sorption by the spodic horizon. Samples were continuously tumbled with an end-over-end shaker during a 24-hour period. The samples of soil suspensions with contact times of 168 and 2016 h, were tumbled by hand every day and every week, respectively. The experiment was performed at an average ambient temperature of 20°C and away from direct light. The CEC was measured on duplicate 2.5 g samples (dry weight basis) after 24 h equilibration time with $C_0$ of 10.1, 20.3, and 101.8 mg P/l. Samples were placed in 25 ml of 0.1 M KCl solution, tumbled for 5 minutes, centrifuged and supernatant discarded; and then this process was repeated. Afterwards, sediment samples were placed in 25 ml of 1.0 N $BaCl_2$ solution, tumbled centrifuged, and the amount of K in the supernatant was measured. The pH was measured in each sample before and after the contact period using an Orion Research Ionalyzer (model 601 A) and an Orion combination pH electrode (Ross 8103). The electrical conductivity (EC) was measured (Rhue and Kidder, 1983) in each P-laden sample and at each solution-to-soil ratio using a Radiometer (model CDM 3). At the end of each contact period the solution was separated by gravity filtration (Whatman No. 42 filter paper). The solution was analyzed for P, Ca, and Al concentrations. The amount of P in solution was determined colorimetrically (John, 1970). The amounts of Ca and Al were determined by the IFAS Analytical Laboratory (Gainesville, FL) with the use of the Inductively Coupled Argon Plasma Spectrometer ICAP. The initial total and Mehlich I extractable P were 25.2 and 3.4 mg/kg soil, respectively.

## Results and Discussion

The concentration of P (C) in solution (from Chapter III, where $\blacktriangle C$ is equal to C in this chapter) and the net amount of P sorbed per kg of soil ($\blacktriangle S$, where $\blacktriangle S=S-S_i$ and $S_i$ is the initial concentration of P in the soil) resulting from changes in initial P concentration, contact period, and soil solids concentration are presented in Tables 4-1 and 4-2. The P concentration in solution (C) decreased very fast during the first 0.5-h period, followed by a slower P sorption reaction. The values of C increased with an increase in $C_o$ and decreased with an increase in soil solids concentration. It is important to mention that the values presented as the net amount of P sorbed per kg of soil are calculated from the P concentration in solution and thus were not independently measured. The amount of P sorbed per kg of soil increased with an increase in time, an increase in $C_o$, and a decrease in soil solids mass. However, the amount of P sorbed per kg of soil increased with an increase in the amount of solids in solution, if the initial amount

Table 4-1. P concentration in solution as affected by equilibration time, soil solids mass, and initial P concentration for a spodic horizon.

| SOIL SOLIDS MASS (g) | TIME (h) | INITIAL P CONCENTRATION (mg/l) | | | | | |
|---|---|---|---|---|---|---|---|
| | | 10.1 | 20.3 | 40.2 | 62.4 | 79.8 | 101.8 |
| | | SOLUTION P (mg/l) | | | | | |
| 12.50 | 0.5 | 0.23 | 0.15 | 0.88 | 1.81 | 4.34 | 6.21 |
| | 1 | 0.23 | 0.05 | 0.50 | 1.40 | 2.75 | 4.33 |
| | 2 | 0.23 | 0.03 | 0.46 | 1.22 | 2.12 | 3.35 |
| | 5 | 0.24 | 0.02 | 0.35 | 1.14 | 1.60 | 3.62 |
| | 24 | 0.14 | 0.15 | 0.00 | 0.00 | 1.41 | 2.82 |
| | 168 | 0.13 | 0.28 | 0.00 | 0.00 | 1.41 | 2.63 |
| | 2016 | 0.12 | 0.20 | 0.49 | 0.74 | 1.28 | 1.99 |
| 6.25 | 0.5 | 0.45 | 0.91 | 5.25 | 11.12 | 15.92 | 28.09 |
| | 1 | 0.39 | 0.68 | 3.05 | 8.52 | 13.70 | 24.96 |
| | 2 | 0.36 | 0.44 | 2.67 | 7.08 | 12.10 | 23.55 |
| | 5 | 0.36 | 0.43 | 2.44 | 5.68 | 10.01 | 19.79 |
| | 24 | 0.14 | 0.43 | 2.21 | 4.92 | 8.02 | 16.92 |
| | 168 | 0.10 | 0.31 | 2.11 | 3.75 | 8.64 | 14.97 |
| | 2016 | 0.22 | 0.40 | 1.54 | 3.09 | 6.59 | 13.12 |
| 4.17 | 0.5 | 0.87 | 2.22 | 10.57 | 20.34 | 33.15 | 48.83 |
| | 1 | 0.70 | 1.60 | 8.71 | 17.08 | 24.96 | 46.03 |
| | 2 | 0.62 | 1.26 | 7.28 | 15.65 | 23.39 | 41.16 |
| | 5 | 0.56 | 1.09 | 5.95 | 13.87 | 21.53 | 38.81 |
| | 24 | 0.31 | 1.05 | 4.96 | 11.23 | 19.91 | 34.33 |
| | 168 | 0.30 | 0.72 | 4.24 | 9.86 | 17.82 | 29.86 |
| | 2016 | 0.33 | 0.77 | 3.22 | 7.43 | 15.45 | 23.88 |
| 3.13 | 0.5 | 1.38 | 3.44 | 16.55 | 25.06 | 41.52 | 56.40 |
| | 1 | 1.10 | 3.06 | 13.87 | 22.11 | 38.08 | 54.43 |
| | 2 | 0.92 | 2.62 | 11.43 | 21.16 | 36.90 | 51.19 |
| | 5 | 0.80 | 1.86 | 9.07 | 19.49 | 34.44 | 47.16 |
| | 24 | 0.41 | 1.76 | 8.31 | 16.41 | 31.32 | 44.70 |
| | 168 | 0.34 | 1.42 | 7.06 | 14.74 | 28.69 | 39.45 |
| | 2016 | 0.45 | 1.14 | 5.66 | 12.60 | 25.15 | 36.46 |
| 2.50 | 0.5 | 2.05 | 5.36 | 17.32 | 30.32 | 46.14 | 63.38 |
| | 1 | 1.45 | 4.81 | 15.80 | 27.14 | 44.99 | 62.00 |
| | 2 | 1.21 | 3.91 | 14.65 | 26.16 | 43.34 | 59.05 |
| | 5 | 1.12 | 3.25 | 12.33 | 23.50 | 39.95 | 56.15 |
| | 24 | 0.67 | 2.35 | 11.04 | 21.80 | 38.84 | 51.54 |
| | 168 | 0.53 | 2.17 | 10.22 | 19.72 | 35.55 | 46.82 |
| | 2016 | 0.60 | 1.73 | 8.71 | 17.89 | 32.90 | 45.14 |

Table 4-2. The effect of soil solids mass, equilibration time, and the initial P concentration on P sorbed by a spodic horizon.

| SOIL SOLIDS MASS (g) | TIME (h) | INITIAL P CONCENTRATION (mg/l) | | | | | |
|---|---|---|---|---|---|---|---|
| | | 10.1 | 20.3 | 40.2 | 62.4 | 79.8 | 101.8 |
| | | SORBED P (mg/kg soil) | | | | | |
| 12.50 | 0.5 | 19.8 | 40.4 | 78.7 | 121.2 | 150.9 | 191.1 |
| | 1 | 19.8 | 40.6 | 79.5 | 122.0 | 154.1 | 194.9 |
| | 2 | 19.8 | 40.6 | 79.5 | 122.4 | 155.4 | 196.8 |
| | 5 | 19.8 | 40.6 | 79.8 | 122.5 | 156.4 | 196.3 |
| | 24 | 20.0 | 40.4 | 80.5 | 124.8 | 156.8 | 197.9 |
| | 168 | 20.0 | 40.1 | 80.5 | 124.8 | 156.8 | 198.3 |
| | 2016 | 20.0 | 40.3 | 79.5 | 123.3 | 157.0 | 199.6 |
| 6.25 | 0.5 | 38.7 | 77.7 | 139.9 | 205.1 | 255.5 | 294.7 |
| | 1 | 38.9 | 78.6 | 148.7 | 215.5 | 264.4 | 307.3 |
| | 2 | 39.1 | 79.6 | 150.2 | 221.3 | 270.8 | 312.9 |
| | 5 | 39.1 | 79.6 | 151.2 | 226.9 | 279.1 | 327.9 |
| | 24 | 39.9 | 79.6 | 152.1 | 229.9 | 287.1 | 339.4 |
| | 168 | 40.1 | 80.1 | 152.5 | 234.6 | 284.6 | 347.2 |
| | 2016 | 39.6 | 79.8 | 154.8 | 237.2 | 292.8 | 354.6 |
| 4.17 | 0.5 | 55.5 | 108.7 | 178.0 | 252.4 | 279.8 | 317.6 |
| | 1 | 56.5 | 112.5 | 189.2 | 271.9 | 329.0 | 334.5 |
| | 2 | 57.0 | 114.5 | 197.7 | 280.5 | 338.4 | 363.7 |
| | 5 | 57.4 | 115.5 | 205.7 | 291.2 | 349.6 | 377.8 |
| | 24 | 58.9 | 115.7 | 211.6 | 307.0 | 359.3 | 404.6 |
| | 168 | 58.9 | 117.8 | 215.9 | 315.3 | 371.9 | 431.5 |
| | 2016 | 58.7 | 117.5 | 222.1 | 329.9 | 386.1 | 467.3 |
| 3.13 | 0.5 | 69.9 | 135.2 | 189.4 | 298.8 | 306.2 | 363.0 |
| | 1 | 72.2 | 138.2 | 210.9 | 322.4 | 333.7 | 378.7 |
| | 2 | 73.6 | 141.8 | 230.4 | 329.9 | 343.1 | 404.6 |
| | 5 | 74.6 | 147.8 | 249.3 | 343.3 | 362.8 | 436.9 |
| | 24 | 77.7 | 148.6 | 255.4 | 367.9 | 387.8 | 456.6 |
| | 168 | 78.3 | 151.4 | 265.4 | 381.3 | 408.8 | 498.6 |
| | 2016 | 77.4 | 153.6 | 276.6 | 398.4 | 437.2 | 522.5 |
| 2.50 | 0.5 | 80.7 | 149.8 | 229.2 | 320.9 | 336.6 | 383.9 |
| | 1 | 86.7 | 155.3 | 244.4 | 352.7 | 348.1 | 397.7 |
| | 2 | 89.2 | 164.4 | 255.8 | 362.5 | 364.5 | 427.2 |
| | 5 | 90.0 | 171.0 | 279.1 | 389.0 | 398.5 | 456.2 |
| | 24 | 94.5 | 179.9 | 292.0 | 406.1 | 409.5 | 502.4 |
| | 168 | 96.0 | 181.8 | 300.1 | 426.8 | 442.4 | 549.6 |
| | 2016 | 95.3 | 186.1 | 315.3 | 445.1 | 469.0 | 566.3 |

of P per gram of soil were equal. Most of the P sorbed per kg of soil reacted in the first half-hour, for all solid concentrations and initial P concentrations. After 0.5 h, teemporalchanges in P sorbed per kg of soil were relatively small. Phosphorus continued to be sorbed slowly only for samples with low soil solids concentrations and large $C_0$, because these samples had enough available P in solution to continue with the sorption reaction. Although the objectives of this experiment were to measure the fast and slow reactions of P, the contact times chosen were not small enough to adequately determine the actual rate of the fast reaction. Detailed description of the effect of $C_0$, time, and soil solids concentration will be given later during the discussion of isotherms and rates.

A modified pseudo-Freundlich equation (the term pseudo- was used because the data are not obtained at equilibrium), used in Chapter 2 ($\blacktriangle S=KC^{n}$), wassfitted to the data of Tables 4-1 and 4-2 for each contact time and soil solid mass. The coefficients K, n, and the correlation coefficients ($r^2$) for each solid concentration and contact period are presented in Table 4-3. The correlation coefficient value significant at the level of probability of 0.1% is 94.9%. In general, the correlation coefficients of the fitted equations were higher than 95%, with the exception for the solid concentration of 12.50. These low $r^2$ values were related to the large analytical error associated with measuring low

Table 4-3. The Pseudo-Freundlich sorption isotherm (given as equation [3-2] fitted parameters, K and n, and the correlation coefficients as affected by contact time and solution:soil ratios for a spodic horizon.

| SOIL SOLIDS MASS (g) | TIME (h) | K (l/kg) | n | $r^2$ (%) |
|---|---|---|---|---|
| 12.50 | 0.5 | 75.49 | 0.520 | 86.3 |
| | 1 | 93.50 | 0.418 | 68.7 |
| | 2 | 97.93 | 0.542 | 72.6 |
| | 5 | 102.91 | 0.474 | 63.5 |
| | 24 | 109.01 | 0.668 | 92.3 |
| | 168 | 105.03 | 0.774 | 98.9 |
| | 2016 | 132.17 | 0.791 | 96.0 |
| 6.25 | 0.5 | 67.04 | 0.463 | 96.6 |
| | 1 | 77.36 | 0.466 | 95.8 |
| | 2 | 87.12 | 0.445 | 93.0 |
| | 5 | 90.46 | 0.478 | 93.0 |
| | 24 | 106.65 | 0.447 | 98.6 |
| | 168 | 118.29 | 0.418 | 98.1 |
| | 2016 | 111.20 | 0.519 | 95.6 |
| 4.17 | 0.5 | 66.91 | 0.417 | 97.7 |
| | 1 | 77.40 | 0.421 | 96.2 |
| | 2 | 84.75 | 0.422 | 96.3 |
| | 5 | 91.16 | 0.425 | 95.8 |
| | 24 | 105.27 | 0.410 | 98.7 |
| | 168 | 114.54 | 0.415 | 97.6 |
| | 2016 | 116.91 | 0.464 | 97.3 |
| 3.13 | 0.5 | 68.39 | 0.415 | 94.5 |
| | 1 | 76.62 | 0.415 | 97.2 |
| | 2 | 85.02 | 0.408 | 97.8 |
| | 5 | 96.85 | 0..401 | 96.3 |
| | 24 | 114.86 | 0.374 | 98.8 |
| | 168 | 125.59 | 0.378 | 98.9 |
| | 2016 | 126.54 | 0.412 | 97.3 |
| 2.50 | 0.5 | 64.38 | 0.444 | 97.9 |
| | 1 | 78.67 | 0.409 | 97.9 |
| | 2 | 88.93 | 0.395 | 98.1 |
| | 5 | 95.97 | 0.406 | 97.4 |
| | 24 | 119.27 | 0.367 | 98.1 |
| | 168 | 128.36 | 0.374 | 98.6 |
| | 2016 | 131.75 | 0.391 | 97.8 |

concentrations of P in solution. The calculated n values were not affected by the different soil solids concentrations and contact times. The average value for n plus or minus one standard deviation was 0.432 ± 0.0772. The small effect of the soil solid concentration was due to the existing relationship between solution and sorbed P, and probably due to the independent measurement of the latter (sorbed P). It was observed that the best fitted K values did not change greatly with different solid concentration, however, the K values were affected significantly by contact time. The K values measured during the first 24 h showed the largest change with time. The values increased by approximately 38% for all soil solid masses. After 2016 h (3 months) of contact time, the K values were still changing but at slower rates. The values of K increased by approximately 10% for all the soil solid masses. The relation between K and contact time was better represented by a nonlinear equation: $K=81.727\ t^{0.0502}$ ($r^2 = 80.7\%$). Time is an important factor when isotherms are used to describe sorption during flow in soil columns or profiles, e.g. where non-equilibrium conditions exist, as under field conditions. The data indicate that during non-equilibrium (short times) the isotherm coefficients (K and n values) were smaller than the ones closer to equilibrium (longer time), and the values continued to change because the soil continued to sorb P. In other words, at short contact times, the amount of P sorbed per kg of soil is smaller than at longer times and larger travel distance will be expected. A modified pseudo-Freundlich equation was fitted to all the data within each time and the coefficients are presented in Table 4-4. Although K values increased with time, the n values did not change with time. The K values increased with time, because the net amount of P sorbed, $\Delta S$, also increased with time. The fitted K values were related to the amount of P sorbed per kg of soil, and any factor that affected P sorbed per kg of soil, such as time, will affect the K values. All the data were also successfully fitted to one equation. The resulting n and K values were 0.418 and 93.86 l/kg. The correlation coefficient value was 87.6 and statistically significant ($P<0.05$). It was observed from the above isotherms that any source of change that affected the concentration of P in solution (C) will affect the concentration of P in sorbed phase (S) in the same way and proportionally because for each soil there appears to be a unique nonlinear relationship between C and S. This relationship could explain the nonlinear behavior between amount of P in solution or sorbed per kg of soil and time, initial applied concentration, and soil solid concentrations described below.

The sorption rate was influenced by the contact time and the $C_0$. The sorption rate ($\Delta S/\Delta t$) is defined as the amount of P sorbed per unit time (h). It was observed from

Table 4-4. The Pseudo-Freundlich adsorption isotherm (equation [3-2]) fitted parameters, K and n, and the correlation coefficients as affected by equilibration time. All data for each solid concentration were grouped together.

| CONTACT TIME (h) | K (l/kg) | n | $r^2$ (%) |
|---|---|---|---|
| 0.5 | 69.08 | 0.427 | 93.7 |
| 1 | 83.58 | 0.399 | 90.5 |
| 2 | 87.39 | 0.416 | 90.8 |
| 5 | 94.55 | 0.421 | 89.7 |
| 24 | 101.79 | 0.435 | 94.8 |
| 168 | 108.26 | 0.445 | 93.8 |
| 2016 | 111.70 | 0.480 | 94.1 |
| ALL | 93.86 | 0.418 | 87.6 |

the data presented in Table 4-2 that the rate of sorption decreased with time. And, the largest rate was observed to occur during the first 0.5-h period of the experiment. Also, for the first 0.5 h, the rates increased with a decrease in the soil solids concentration and initial P concentration. Using the calculated relationship between K and t and between S and C (Table 4-4), the sorption rate could be approximated by the following empirical equation:

$$\Delta S/\Delta t=4.1\ t^{-0.95}\ C^{0.42} \qquad [4\text{-}1]$$

This equation shows that increasing contact time or decreasing the equilibrium concentration decreases the sorption rate. It was observed that for the case with 12.5 g of soil, almost all the P initially in solution was sorbed during the first 0.5 h. Also, the increase in the sorption rate with a decrease in soil solids concentration was not proportional and was probably influenced by the nonlinear relation between solution and sorbed phases. Reaction rates have been shown to depend upon the collision (or encounter) frequency (Atkins, 1982) between the solid and sorbate. An increase in solid or sorbate (P in solution) should therefore increase the number of encounters and the reaction rate. However, the data show here that rates for P reaction are positively influenced by initial concentration of P in solution but not the solid concentration.

Results obtained here were similar to results obtained earlier by Kanchanasut (1974) with soil material from a Bh horizon near Fort Pierce, Florida. The data showed that the fast reaction was over before the first half hour and appeared to be comparable with a ligand exchange reaction (Furumai and Ohgaki, 1988). And, the reaction was related rate to the concentration of solids (Chen et al., 1973). The slow reaction was related to a diffusion (Willet et. al., 1988) or precipitation (van Riemsdijk et. al., 1984) mechanism, both of them time-dependent reactions.

During most batch study experiments, researchers are primarily interested in measuring changes of P concentration in solution. However, little attention has been given to changes in concentration of other solutes that directly or indirectly can be related to P removal from solution. During this experiment, pH, Ca, and Al concentrations were measured in samples. Ca and Al were chosen to be monitored because of the formation of relatively low solubility phosphatic compounds in soils. The pH of the soil suspensions were measured before and after each contact period (Table 4-5). The pH did not change significantly with different soil solids concentrations, $C_o$, and contact times. The average pH values before and after each contact period were 4.01 with a standard deviation of 0.14, and 4.06 with a standard deviation of 0.12. The pH values are similar to ones reported in the literature as characteristic of the Bh horizon (Chapter 1), and the small change in the pH was due to the high acid-buffering capacity of the Bh

Table 4-5. Final pH as affected by soil solids concentration, equilibration time, and initial P concentration.

| SOIL SOLIDS MASS (g) | TIME (h) | INITIAL P CONCENTRATION (mg/l) | | | | | |
|---|---|---|---|---|---|---|---|
| | | 10.1 | 20.3 | 40.2 | 62.4 | 79.8 | 101.8 |
| 12.50 | 0.5 | 3.94 | 4.00 | 4.00 | 3.94 | 3.97 | 3.91 |
| | 1 | 3.98 | 3.97 | 3.99 | 3.96 | 3.89 | 3.89 |
| | 2 | 3.92 | 3.96 | 3.94 | 3.97 | 3.95 | 3.86 |
| | 5 | 3.89 | 3.76 | 3.74 | 3.88 | 3.97 | 3.73 |
| | 24 | 3.82 | 3.73 | 3.91 | 4.02 | 3.86 | 3.74 |
| | 168 | 3.84 | 3.82 | 3.92 | 3.92 | 4.03 | 4.16 |
| | 2016 | 4.01 | 4.03 | 4.03 | 4.06 | 4.12 | 4.08 |
| 6.25 | 0.5 | 4.02 | 4.04 | 4.04 | 4.02 | 4.03 | 3.95 |
| | 1 | 4.04 | 4.01 | 4.03 | 4.10 | 4.07 | 3.97 |
| | 2 | 4.02 | 4.06 | 4.02 | 4.07 | 4.05 | 3.94 |
| | 5 | 4.03 | 3.89 | 3.91 | 3.99 | 3.99 | 3.88 |
| | 24 | 3.92 | 3.93 | 4.01 | 4.05 | 3.78 | 3.91 |
| | 168 | 3.95 | 3.96 | 4.07 | 4.07 | 4.24 | 4.27 |
| | 2016 | 4.15 | 4.15 | 4.19 | 4.20 | 4.19 | 4.21 |
| 4.17 | 0.5 | 4.08 | 4.07 | 4.15 | 4.10 | 4.16 | 3.98 |
| | 1 | 4.09 | 4.05 | 4.08 | 4.06 | 4.22 | 4.00 |
| | 2 | 4.08 | 4.13 | 4.09 | 4.07 | 4.13 | 4.00 |
| | 5 | 4.05 | 3.98 | 4.08 | 4.07 | 4.09 | 3.99 |
| | 24 | 3.97 | 3.94 | 4.05 | 4.07 | 3.88 | 3.96 |
| | 168 | 4.09 | 4.02 | 4.21 | 4.14 | 4.25 | 4.30 |
| | 2016 | 4.19 | 4.20 | 4.23 | 4.23 | 4.21 | 4.22 |
| 3.13 | 0.5 | 4.12 | 4.12 | 4.10 | 4.06 | 4.23 | 3.98 |
| | 1 | 4.09 | 4.09 | 4.14 | 4.13 | 4.17 | 4.04 |
| | 2 | 4.08 | 4.09 | 4.10 | 4.03 | 4.15 | 4.01 |
| | 5 | 4.04 | 4.02 | 4.11 | 4.02 | 4.13 | 3.99 |
| | 24 | 3.98 | 4.01 | 4.10 | 4.07 | 3.96 | 4.00 |
| | 168 | 4.09 | 4.05 | 4.17 | 4.24 | 4.29 | 4.32 |
| | 2016 | 4.24 | 4.23 | 4.24 | 4.25 | 4.25 | 4.23 |
| 2.50 | 0.5 | 4.12 | 4.11 | 4.14 | 4.13 | 4.26 | 4.07 |
| | 1 | 4.14 | 4.19 | 4.10 | 4.12 | 4.25 | 4.00 |
| | 2 | 4.12 | 4.11 | 4.11 | 4.10 | 4.19 | 4.02 |
| | 5 | 4.05 | 4.06 | 4.07 | 4.07 | 4.12 | 4.06 |
| | 24 | 4.02 | 4.09 | 4.09 | 4.08 | 4.02 | 4.13 |
| | 168 | 4.16 | 4.09 | 4.22 | 4.26 | 4.28 | 4.31 |
| | 2016 | 4.26 | 4.23 | 4.27 | 4.25 | 4.25 | 4.23 |

horizon. The EC values measured in the P-laden solutions ranged from 1.5 ($C_0$=10.1 mg P/l) to 1.7 ($C_0$=101.8 mg P/l) dS/m. The EC value measured for suspensions with different soil solids concentrations ranged from 0.1 (12.5 g soil) to 0.04 (2.5 g soil) dS/m. As shown, the total electrolyte (salt) content of the applied solution was at least 15 times larger than the salt content originally in the solution equilibrated with the soil. Thus, in general, these data indicate that any salt content effect due to change in solid concentration will be relatively small compared to that due to change in the applied solution. Furthermore, the effect of different initial P concentrations on the total salt content or ionic strength of the solutions was in the order of 12% between solutions having initial P concentration of 10 and 100 mg P/l. These small changes in ionic strength were assumed not to be a major part of the effect of different $C_0$ upon P sorption. Bar-Yosef et al. (1988) found that increasing EC from 0.2 to 5 dS/m increased P sorption by Ca- and K- saturated kaolinite for pH around 7. However, at pH of 5, an increase in EC did not affect P sorption. Also, Hsu (1977) observed that the adsorption of specifically-sorbed ions is relatively insensitive to changes in ionic strength.

The data for Ca released by the soil (mg/kg), from 0.5 to 168 h, are presented in Table 4-6. Ca was apparently released from the soil by cation exchange reaction with

Table 4-6. Average calcium released by a spodic horizon during P sorption as affected by time, soil solids concentration, and initial P concentration.

| SOIL SOLID MASS (g) | TIME (h) | INITIAL P CONCENTRATION | | | | | |
|---|---|---|---|---|---|---|---|
| | | 10.1 | 20.3 | 40.2 (mg/l) | 62.4 | 79.8 | 101.8 |
| | | | | Ca (mg/kg) | | | |
| 12.50 | 0.5 | 35 | 33 | 28 | 29 | 25 | 25 |
| | 1 | 35 | 33 | 29 | 28 | 25 | 28 |
| | 2 | 36 | 34 | 29 | 29 | 26 | 26 |
| | 5 | 39 | 37 | 32 | 30 | 29 | 26 |
| | 24 | 38 | 38 | 32 | 32 | 30 | 29 |
| | 168 | 37 | 36 | 32 | 31 | 29 | 27 |
| 6.25 | 0.5 | 49 | 44 | 40 | 39 | 38 | 34 |
| | 1 | 53 | 44 | 41 | 39 | 36 | 37 |
| | 2 | 52 | 49 | 42 | 37 | 35 | 35 |
| | 5 | 55 | 48 | 41 | 40 | 38 | 40 |
| | 24 | 58 | 54 | 42 | 42 | 44 | 42 |
| | 168 | 60 | 52 | 41 | 42 | 39 | 38 |
| 4.17 | 0.5 | 63 | 56 | 46 | 44 | 47 | 47 |
| | 1 | 64 | 56 | 48 | 49 | 44 | 42 |
| | 2 | 63 | 61 | 49 | 47 | 47 | 51 |
| | 5 | 70 | 62 | 49 | 47 | 50 | 52 |
| | 24 | 72 | 62 | 77 | 53 | 51 | 50 |
| | 168 | 72 | 64 | 55 | 52 | 51 | 48 |
| 3.13 | 0.5 | 70 | 65 | 64 | 60 | 54 | 62 |
| | 1 | 75 | 66 | 60 | 56 | 62 | 63 |
| | 2 | 74 | 68 | 58 | 60 | 54 | 61 |
| | 5 | 78 | 70 | 60 | 58 | 54 | 64 |
| | 24 | 85 | 70 | 63 | 61 | 65 | 66 |
| | 168 | 78 | 69 | 62 | 61 | 56 | 62 |
| 2.50 | 0.5 | 75 | 71 | 68 | 67 | 70 | 72 |
| | 1 | 86 | 76 | 70 | 72 | 68 | 66 |
| | 2 | 81 | 72 | 72 | 69 | 63 | 66 |
| | 5 | 79 | 81 | 69 | 68 | 73 | 71 |
| | 24 | 89 | 83 | 64 | 72 | 69 | 76 |
| | 168 | 85 | 81 | 68 | 76 | 74 | 71 |

potassium (or $H_3O^+$) or other cations coming into the soil solution (probably Al or organics). The Ca released by the soil was not appreciably affected by the contact time. Surface exchange reactions are virtually instantaneous in a well-mixed or stirred system (Harter and Lehmann, 1983). Exchange reaction rates of K-Ca have been found to be in the order of less than 1 $min^{-1}$ (Ogwada and Sparks, 1986). However, the Ca released was affected by the initial P concentration and the soil solids mass. Decreasing the soil solids mass increased the Ca released by the soil. The Ca released increased linearly (by approximately 2.6 times) but not in proportion from 12.5 to 2.5 g soil (i.e., a 5-fold change) and was the same for all six values of $C_0$. The amount of Ca released ranged from 20 to 30 mg Ca/kg for soil solids mass of 12.5 g and from 60 to 70 mg Ca/kg for soil solids mass of 2.5 g. The increase in Ca release related to a decrease in soil solids mass was probably due to the higher concentration of K in solution (mass action), or to a low solution-Ca concentration (dilution factor). Furthermore, for a given soil solid mass, the Ca released by the soil increased with a decrease in the initial P concentration applied. Between $C_0$ values of 10 and 100, the amount of Ca released decreased by 4% when the soil solids mass was 2.5 g, and by 30% with 12.5 g. These decreases in corresponding amounts of Ca released, could be related to an increase in P sorbed by the soil with decreasing soil mass and increasing $C_0$. The decrease in Ca released could be due to readsorption by the soil or co-precipitation with P. The Ca released by cation exchange should be related to the concentration of K in solution which is higher with increasing $C_0$, but the Ca released decreased. Ca precipitation in solution at pH 4 requires P concentrations in solution on the order of 3,000 mg/l (assuming unity of the activity coefficient), conditions which obviously did not exist during this experiment (Lindsay, 1979). The Ca ions, however, could be readsorbed by the soil during an increase in CEC followed by P sorption (Gillman and Fox, 1980), which is directly related to the amount of P sorbed per kg of soil, as is shown by the data. This effect was more accentuated at high soil solid mass than at low solid mass (larger surface area), which could indicate a surface reaction. No increases in CEC values were observed in this experiment with an increase in $C_0$. The average CEC value plus or minus one standard deviation was 41.7 ± 1.2 mmol/kg soil. However, other surface reactions (e.g., co-precipitation) could also affect the results.

The Al data was highly variable, which limits the usefulness of any conclusions about Al behavior. However, the aluminum released was affected by initial P concentration and contact time (Table 4-7). Soil solids mass had no effect on the amounts of Al released between 6.25 and 2.5 g. However, the difference between this range

Table 4-7. Average Al released by a Bh horizon during P sorption as affected by the equilibration time and initial P concentration.

| SOIL SOLID MASS (g) | TIME (h) | INITIAL P CONCENTRATION | | | | | |
|---|---|---|---|---|---|---|---|
| | | 10.1 | 20.3 | 40.2 | 62.4 | 79.8 | 101.8 |
| | | | | (mg/l) | | | |
| | | | | Al (mg/kg) | | | |
| 12.50 | 0.5 | 2 | 2 | 2 | 2 | 2 | 2 |
| | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| | 2 | 3 | 3 | 2 | 2 | 2 | 3 |
| | 5 | 3 | 3 | 3 | 4 | 4 | 5 |
| | 24 | 5 | 6 | 7 | 14 | 7 | 12 |
| | 168 | 7 | 6 | 6 | 12 | 9 | 13 |
| 6.25 | 0.5 | 2 | 2 | 2 | 2 | 2 | 2 |
| | 1 | 3 | 2 | 2 | 2 | 2 | 2 |
| | 2 | 3 | 3 | 3 | 3 | 3 | 3 |
| | 5 | 4 | 5 | 4 | 5 | 7 | 5 |
| | 24 | 9 | 7 | 11 | 21 | 20 | 18 |
| | 168 | 9 | 13 | 17 | 18 | 20 | 26 |
| 4.17 | 0.5 | 2 | 2 | 2 | 2 | 2 | 2 |
| | 1 | 3 | 2 | 2 | 2 | 2 | 2 |
| | 2 | 4 | 3 | 3 | 4 | 3 | 3 |
| | 5 | 4 | 4 | 2 | 5 | 4 | 5 |
| | 24 | 9 | 13 | 11 | 16 | 17 | 21 |
| | 168 | 16 | 11 | 19 | 23 | 22 | 25 |
| 3.13 | 0.5 | 2 | 2 | 2 | 2 | 2 | 2 |
| | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| | 2 | 3 | 2 | 2 | 3 | 3 | 3 |
| | 5 | 4 | 4 | 4 | 5 | 4 | 4 |
| | 24 | 8 | 14 | 9 | 18 | 14 | 19 |
| | 168 | 8 | 9 | 22 | 25 | 23 | 27 |
| 2.50 | 0.5 | 2 | 1 | 1 | 2 | 2 | 2 |
| | 1 | 2 | 1 | 2 | 2 | 2 | 3 |
| | 2 | 4 | 3 | 3 | 3 | 3 | 4 |
| | 5 | 4 | 4 | 4 | 5 | 4 | 5 |
| | 24 | 8 | 7 | 15 | 12 | 18 | 12 |
| | 168 | 9 | 9 | 19 | 22 | 25 | 28 |

and 12.5 g soil mass was minimal and could be related to analytical errors during sampling or low Al concentration in solution (below detection limit). Released Al (approximately 4 mg/l) was the same for all initial P concentrations for the first 5 h of the experiment. During the 24 and 168 h contact time periods the Al released increased by approximately 15 and 10 mg Al/l, respectively.Also, released Al increased, by 10 to 20 mg Al/l between solutions with $C_0$ values of 10.1 and 101.8 mg P/l, but only during 24 and 168 h contact times. The change in released Al was independent of the P sorption, especially during the fast sorption reaction (highest amount of P sorbed per kg of soil). In general, aluminum concentrations in soil solution are controlled by mineral dissolution reaction and ion exchange or adsorption reactions (Walker et al., 1988). Unless limited by diffusion, the exchange reaction K-Ca should be fast and not be time dependent. However, the dissolution reaction for soil minerals should be time dependent. Bloom and Erich (1987) showed that a low P concentration (3 mg/l) in solution will enhance the dissolution of gibbsite at pH less than 3. Their results suggest that concentration of Al complexing anions in solution may be important in determining the rates of dissolution of aluminous minerals present in the soil. In this investigation, after 5 h, the rates of Al released (approximately 0.4 and 0.04 mg/kg/h for 24 and 168 h) were faster than P sorption (0.1 and 0.01 mg/kg/h, respectively). The Ca and Al released by the soil were affected directly or indirectly by the P sorbed by the soil, but these released cations did not affect the P sorption by the soils. However, precipitation (Ca and Al phosphate) cannot be ruled out due to the unknown form (amorphous) of the precipitated material.

## Conclusion

Stirred suspensions of soil samples in aqueous phosphorus solutions were used to characterize sorption kinetics of a Spodosol Bh horizon. As expected, increasing the initial concentration of P in solution increased the amount of P sorbed per kg of soil and the rate of sorption. With increasing contact time, the amount of P sorbed per kg of soil increased, but the sorption rate decreased. However, decreasing the soil solids mass (soil:solution ratio) increased the amount of P sorbed per kg of soil as well as the sorption rates. The nonlinear relation between S and C influenced the amount of P sorbed while changing $C_0$ and soil solids mass. A unique nonlinear relationship between S and C was believed to exist for each soil. This relationship strongly depended upon contact time as was the case in Chapter III where a constant value of n was found for different soils. Probably, the different values of K could be related to different "equilibrium times" for each of the soils sampled, which also relate to the amount of reactive material found in the soil. Sorption rate values determined in experiments with batch studies, e.g. high solution:soil ratios (>1 ml/g, or low soil solids concentration) will be difficult to extrapolate rate values in column or to in situ field work where these values are typically < 0.3 ml/g. However, for a realistic column solution:soil ratio of < 0.3 ml/g, the initial reaction rate should presumably be very fast (faster than in a batch study) and the reaction should continue slowly over long time periods without reaching an equilibrium. The fitted value for n from a modified Freundlich equation remained relatively constant (0.42) between contact times, soil solids concentrations, and $C_0$. The same value was found for different subsurface horizons in Chapter II. This value could be used in a mathematical model, as a first approach, to describing P movement with water flow through soil columns. It is important to emphasize that K and n parameters used in the Freundlich isotherm provide only a mathematical approach to describe the complex phenomenon of P sorption rather than the actual mechanism.

The pH of the samples remained relatively constant throughout the experiment. The Ca and Al were affected by P sorption directly or indirectly. The reactions of cations released by the soil appear to be ion exchange (Ca) and dissolution (Al). But concentration of these ions in solution were not expected to influence P sorption (e.g., by precipitation). However, under different conditions, these or other ions should influence P sorption processes. It is important to measure other ions (Ca, Al, organic acids, etc.), initially in the soil as well as in solution (during the experiment), especially if these ions influence P reaction with soil during sorption kinetics.

# CHAPTER V
# PHOSPHATE SORPTION AND DESORPTION DURING TRANSPORT WITH WATER IN SMALL SOIL COLUMNS

## Introduction

The miscible displacement technique commonly used (Nielsen and Biggar, 1961) for applying aqueous solutions of chemicals through water saturated soil columns during steady state flow conditions is a useful and realistic procedure to evaluate and describe phosphorus (P) adsorption and desorption phenomena in soils under conditions of water flow. Another technique, the batch isotherm method provides a conventional, non-flow means for evaluating P sorption in well-mixed aqueous suspensions of soil samples. The batch technique however has been shown (Stuanes and Enfield, 1984) to underestimate the maximum sorption capacity of P in comparison with results obtained using miscible displacement with laboratory columns and _in situ_ field investigations. Advantages of the miscible displacement technique over the batch technique include a more realistic soil-to-solution ratio (typically 0.3 g $cm^{-3}$ under field conditions), the initial concentration of P does not change as the reaction proceeds, and desorbed species are continually removed from the vicinity of the reaction sites (Carski and Sparks, 1985), as would occur naturally in a soil profile.

Reaction of P with acid, sandy soils generally involves local non-equilibrium (as shown in Chapter IV for Spodosols) during water flow and only partially reversible processes which primarily occur due to reactions with Fe and Al oxides present in the soil. However, scientists are not in agreement as to the exact number of individual reactions and whether these reactions operate in series or in parallel. Furthermore, experimental techniques are not generally available to monitor all of the specific reactions. A complete mathematical model to thoroughly describe P chemical reactions in soil does not actually exist at the moment, but models which approximate these reactions do exist, however. The rate of adsorption (Chapter III and IV) and/or desorption of P depends upon, amongst other factors, the concentration of P in the soil solution. Also, adsorption and desorption of P have been described as fast, reversible reactions which occur simultaneously with a slower, and practically irreversible reaction (van der Zee et al., 1986). Mathematical models have been used to predict reactions and transport of P and some of them are described in Chapter I.

Bottcher et al. (1986) found that, for soils located at dairies in the watershed north of Lake Okeechobee, manure-loaded areas had extremely high levels of total and Mehlich

I extractable P as compared to soils with native vegetation areas. High levels of P with relatively weak bonding to soil components occurred in the surface horizon, and the subsurface Bh horizon had larger adsorption potential than either the A or E horizons, due to the organic matter and Al contents in the Bh horizon.

Aqueous P solutions with given concentrations were miscible displaced through short soil columns with disturbed (hand packed) soils in order to investigate P adsorption and desorption processes. The objective was to evaluate the influence of sorption/desorption reactions upon P transport with water flow in the soil with the use of observed breakthrough curves (BTCs).

## Materials and Methods

Bulk samples of subsurface horizons (Bh horizon) were collected from profiles of Immokalee (Arenic Haplaquod) and Myakka (Aeric Haplaquod) soil series located at W.F. Rucks, Dry Lake # 1, and Larson # 6 dairies from the Okeechobee county area of southern Florida (Table 5-1). The soil samples were air-dried and sieved (No. 10 sieve with 2-mm openings) prior to use in the experiments. No attempt was made to remove residual P present in the soils.

Soil columns used in the miscible displacement experiments were prepared by hand-packing air-dry soil into acrylic plastic cylinders with 3.78-cm inside diameter and

Table 5-1. Location, depth of the Bh horizon, and Mehlich I (MIP) and total extractable phosphorus (TEP) of soils used in this research.

| DAIRY | DEPTH (cm) | SOIL SERIES | MIP | TEP |
|---|---|---|---|---|
| | | | --- (mg/kg) | --- |
| W.F.Rucks | 51-61 | Myakka | 24.1 | 38.2 |
| Dry Lake # 1 | 84-99 | Immokalee | 6.2 | 12.6 |
| Larson # 6 | 107-137 | Immokalee | 42.4 | 345.8 |

length of 2 cm. The air-dry soil was packed in small increments and the amount of soil used per column (22.4 $cm^3$) was comparable to bulk density values observed under field conditions (1.5 gm $cm^{-3}$). Fine mesh nylon screens (Spectramesh, 70 mesh per micron) were placed over each end of the column to retain the soil particles during water flow through the columns. Acrylic endplates with small internal cavities (20% of the total volume of the column, approximately 4.5 ml) were placed over each screen. A special modification of the commonly-used miscible displacement technique was used here to experimentally examine P mobility in soil columns. Solutions with given P concentration were applied with constant flux to the bottom of a short vertical column until a desired number of pore volumes of effluent were collected. Unsteady, unsaturated water flow occurred during infiltration of the first pore volume of influent solution. However, the unsteady, unsaturated flow condition of the column was assumed to only affect P sorption at the bottom end of the column and primarily only during the first few minutes (first pore volume of influent) of infiltration. The high P sorption buffer capacity of the Bh horizon soil (Chapter III) will retard the P front behind the advancing water front. During that initial period, a relatively sharp (due to net water flow forced in the direction opposite to that of the gravitational field) wetting front advanced upward through the initially air-dry soil, dissolving and moving any soluble salts present on walls of soil pores. Shortly after the wetting front reached the top soil surface, outflow of effluent occurred. Saturated steady flow was established rapidly during the first effluent pore volume, and continued for the duration of infiltration. A designated volume (or pulse) of aqueous electrolyte solutions containing 5, 10, 50, or 100 mg/l of P as $KH_2PO_4$ ($C_0$) was displaced into initially air-dry soil columns (adsorption BTCs). The ionic strength of all four P solutions was maintained constant at 10 mmol/l using KCl. Input flux was maintained essentially constant with a peristaltic pump (model Rabbit, RAININ) and effluent fractions were collected with an automatic fraction collector (ISCO model 270). After application of each phosphorus influent solution, a 10 mmol/l KCl solution without phosphorus was introduced to the bottom endplate of each column (desorption BTCs) until the P concentration in the effluent solution became similar to that of the influent phosphorus solution (more than 95%).

The effluent solution (adsorption and desorption) was collected at different time intervals and the concentration of P was determined for specific samples. Volumes of effluent collected in tubes in the fraction collector were measured. The measured volume (per time) was used to calculate pore volume of effluent (i.e. the volume of liquid in the saturated soil column) and liquid application rate.

Effluent was collected until the P concentration in the effluent was 10% or less of the initial P concentration. After completing each column run, the wet-soil columns were weighed to calculate the pore volume for each column. The concentration of P in the effluent was determined by the ascorbic acid-molybdenum blue colorimetric method (John, 1970). Concentrations of P in the effluent relative to influent concentrations were plotted against measured pore volume of effluent for the adsorption and desorption BTCs.

Physical parameters investigated for the soil columns are summarized in Table 5-2. Average values for soil bulk density and pore volume used during these experiments were 1.56 g/ml (with a corresponding standard deviation of 0.101) and 10.36 ml (standard deviation of 1.00), respectively. Pulses of nonreactive electrolyte solution containing tritiated water ($^3H_2O$) were used to obtain breakthrough curves (step function) on selected soil columns. Radioactivity of applied pulses of $^3H_2O$ was 0.2 nCi/ml in aqueous solution. The tritiated water was applied to columns after the P desorption BTCs were terminated, under the same water flow condition (saturated water content, steady flow, and pore water velocity). Dispersion coefficients were calculated by least square fitting the Parker and van Genuchten model (1984) to observed BTCs for $^3H_2O$.

TABLE 5-2. Description of experimental soil columns used for miscible displacement of solution with P concentration.

| LOCATION | COLUMN # | BULK DENSITY ($g/cm^3$) | PORE VOLUME (ml) | $C_o$ (mg/l) | SOLUTION APPLICATION RATE (cm/h) | SATURATED WATER CONTENT ($cm^3/cm^3$) |
|---|---|---|---|---|---|---|
| W.F.RUCKS | 1 | 1.55 | 9.49 | 96.79 | 2.55 | 0.41 |
| | 2 | 1.50 | 10.49 | 51.15 | 2.57 | 0.45 |
| | 3 | 1.51 | 10.19 | 10.68 | 2.59 | 0.44 |
| | 4 | 1.45 | 11.25 | 4.87 | 2.41 | 0.48 |
| DRY LAKE | 5 | 1.61 | 9.28 | 101.71 | 2.55 | 0.40 |
| | 6 | 1.61 | 9.84 | 51.15 | 2.69 | 0.42 |
| | 7 | 1.62 | 10.18 | 10.68 | 2.64 | 0.43 |
| | 8 | 1.55 | 11.07 | 4.87 | 2.71 | 0.47 |
| LARSON | 9 | 1.45 | 10.43 | 101.71 | 2.45 | 0.45 |
| | 10 | 1.53 | 9.90 | 51.15 | 2.45 | 0.42 |
| | 11 | 1.54 | 9.85 | 10.68 | 2.41 | 0.42 |
| | 12 | 1.53 | 9.94 | 4.87 | 2.38 | 0.42 |

## Results and Discussion

The Bh horizons were collected in pasture lands located in the vicinity of the milking barns for each of three dairies. These soils had been influenced differentially (soil phosphorus concentration) by P contained in manure and urine from dairy cows. Mehlich I and total extractable P (Table 5-1) levels in the soils show phosphorus concentrations that ranged approximately from 6 to 40 mg P/kg and 10 to 350 mg P/kg, respectively. The variability in P concentration was related to relative position in the landscape and variability (temporal and spatial) in cow density (# of cows per unit land area) (see Chapter 2). The soil bulk density ranged from 1.45 to 1.62 g/cm with an average of 1.54 ± 0.06 g/cm, and solution application rate ranged from 2.38 to 2.69 cm/h with an average of 2.53 ± 0.11 cm/h (Table 5-2). Bulk density values and application rates were maintained relatively constant for the column experiments. Pore volummeand final water content (pore volume divided by total volume) were calculated by differences in weight before and after miscible displacement experiments with the columns. The average plus or minus one standard deviation for the magnitude of one pore volume values were 10.2 ± 0.58 cmU$^3$. The initial water content of the soil was less than 1% (air dry soil, or < 0.04 cm$^3$/cm$^3$) for all three soils. The P concentration in the effluent divided by the P concentration applied $C_o$ in the influent were plotted against pore volumes of effluent to give BTCs. The calculated average dispersion coefficient for the three Bh horizons (8 columns) was 117.2 ± 92.5 $cm^2$/day. The relative concentration of 0.5 occurred after 0.98 pore volume of effluent which is close to the theoretical breakthrough point for nonreactive solute (1 pore volume).

As was observed in experimental BTCs for P reported by Selim et al. (1974) and Mansell et al. (1977) for A and Bh horizons, experimental data reported here were retarded and asymmetric with excessive tailing during adsorption and desorption BTCs. General shape of the P BTCs were related to (1) a nonlinear relation between P in the solution and sorbed phases, also observed in Chapter III and IV (Freundlich sorption isotherm), and (2) a nonequilibrium relation between sorption and time, also observed in Chapter IV (kinetics, fast and slow reaction). Both of which are characteristics for P reactions with soil components. Observed adsorption P BTC's for columns of the Bh horizon soils collected at Rucks dairy, for different phosphorus concentrations ($C_o$ of 100, 50, 10, and 5 mg P/l) of influent, are shown in Figure 5-1. For the Bh horizon, when the influent P concentrations were 50 and 100 mg/l, P appeared in the effluent solution before two pore volumes had been collected and for applied-P concentrations of 5 and 10 mg/l, P did not occur in the effluent solution before the

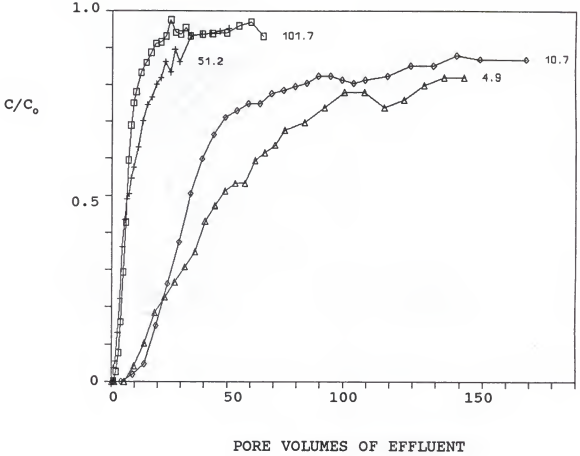


Figure 5-1. Adsorption BTCs for P effluent from soil columns from Rucks Bh horizon with different $C_0$ (101.7, 51.2, 10.7, 4.9 mg P/l) applied.

first ten pore volumes. The relative mobility for the applied P increased with the increase in $C_0$. Using a relative P concentration $C/C_0$ of 0.5 as an arbitrary reference, larger numbers of displacing pore volumes were needed to reach that concentration in column effluent for smaller $C_0$. For strictly steady, saturated flow conditions, $C/C_0 = 0.5$ for a conservative or nonreactive solute, theoretically, should occur at 1 pore volume of effluent. However, under experimental conditions used here, a condition of unsteady, unsaturated water flow occurred between initiation of constant-flux infiltration of P solution into air-dry soil and initiation of effluent outflow from the soil column. This period was relatively short in time and was followed by a steady, saturated flow conditions soon after effluent flow started. Under the conditions of the experiment, $C/C_0 = 0.5$ for a conservative or nonreactive solute should occur at 0 pore volume of effluent. However, for reactive solutes such as P, the number of pore volumes of effluent needed to reach $C/C_0 = 0.5$ were 6.6, 7.6, 33.8, 47.9 for initial P concentrations of 96.8, 51.2, 10.7, and 4.9 mg P/l, respectively. Considerable tailing of BTCs was observed so that $C/C_0$ did not actually reach unity during these experiments, even after 50 to 300 pore volumes, depending upon $C_0$. This also influences interpretation of desorption BTCs. A relative concentration of 0.9 was attained only with influent concentrations of 50 and 100 mg P/l and only after 19 and 27 pore volumes, respectively. Desorption (P-free influent applied) BTCs for columns of Bh horizon soils collected at Rucks dairy are shown in Figure 5-2. A value for $C/C_0$ of 0.5 was obtained, for the Bh columns, within the first three pore volumes after terminating application of influent with P concentrations of 100 and 50 mg/l. For the other two influent P concentrations (5 and 10 mg/l), ten pore volumes had to be displaced to reach the same relative concentration ($C/C_0$) of 0.5. To decrease the relative P concentration in the effluent to 0.1, the number of displaced pore volumes ranged from 10 to 70 for $C_0$ values ranging from 100 to 5 mg P/l, respectively, requiring more cumulative flow for the smaller $C_0$ solution. This increase in the number of pore volumes of effluent displaced as the influent P concentration was decreased is due to nonlinearity of sorption/desorption and to a slow kinetic reaction process that tends to be characteristic of P in such soils. Concentration of P observed in the initial column effluent was zero which implies the irreversibility of the P initially present in the soil. Also, the desorption BTCs start below $C/C_0 = 1$ because the adsorption BTCs did not reach the value of $C_0$.

Adsorption and desorption BTCs for columns of Bh soil horizons collected at Dry Lake and Larson dairies are shown in Figs. 5-3 and 5-4, and Figs. 5-5 and 5-6, respectively.

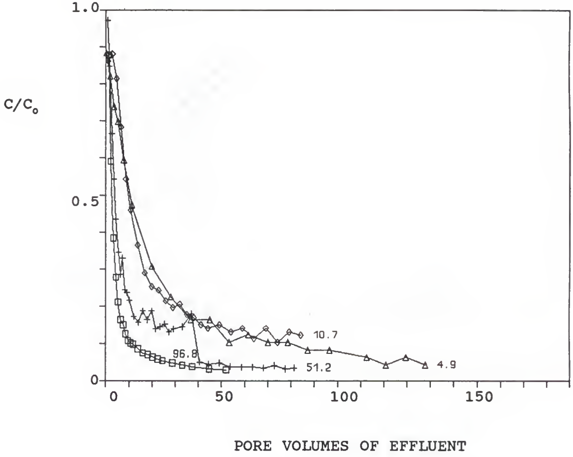


Figure 5-2. Desorption BTCs for P effluent from soil columns from Rucks Bh horizon with 0.01 M KCl after the application of differents $C_0$ (101.7, 51.2, 10.7, 4.9 mg P/l).

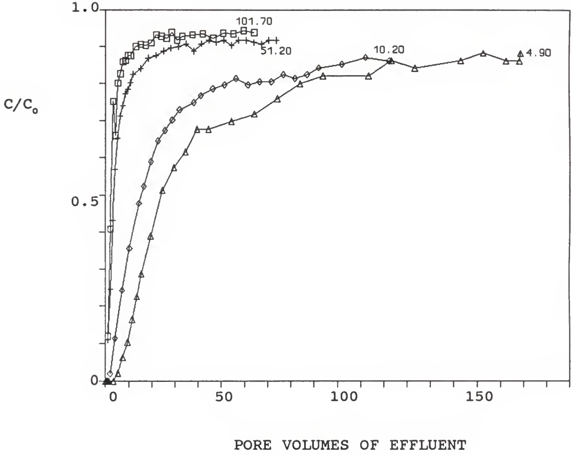
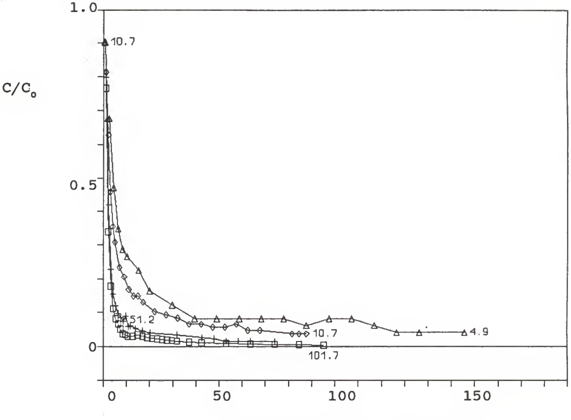


Figure 5-3. Adsorption BTCs for P effluent from soil columns from Dry Lake Bh horizon with different $C_0$ (101.7, 51.2, 10.7, 4.9 mg P/l) applied.



PORE VOLUMES OF EFFLUENT

Figure 5-4. Desorption BTCs for P effluent from soil columns from Dry Lake Bh horizon with 0.01 M KCl after the application of different $C_0$ (101.7, 51.2, 10.2, 4.9 mg P/l).

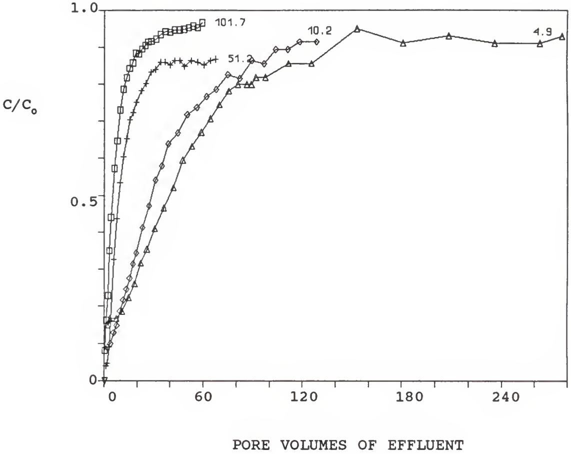


Figure 5-5. Adsorption BTCs for P effluent from soil columns from Larson Bh horizon with different $C_o$ (101.7, 51.2, 10.2, 4.9 mg P/l) applied.

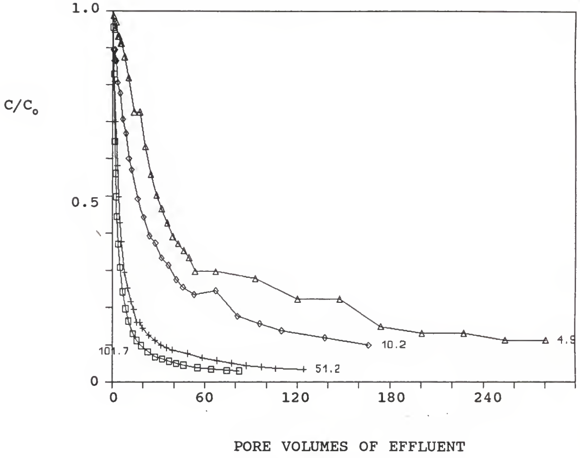


Figure 5-6. Desorption BTCs for P effluent from soil columns from Larson Bh horizon with 0.01 KCl after the application of differents $C_o$ (101.7, 51.2, 10.2, 4.9 mg P/l).

BTCs for all three soils showed similar nonequilibrium and nonlinear reaction behavior. For the miscible displacement adsorption experiments with columns of soils from all three Bh horizons, the number of pore volumes needed to increase the relative P concentration in the effluent solution by 0.5 or 0.9 for net sorption conditions, or to reduce it by 0.5 or 0.1 for net desorption conditions, increased as the influent P concentration was decreased due to the nonlinear behavior (as shown by the batch experiments in Chapter III and IV) of the P reaction in solution with the soil. Differences in shape of BTCs between the different soils were not related to differences in the initial P concentration in the soil (Table 5-1). Larson's Bh horizon had 10 times more TEP than Rucks' Bh and yet P BTCs for these two soils were similar. Obviously the presence of residual P in these soils had little effect upon mobility of applied aqueous P solutions. Also, the Bh horizon from Dry Lake dairy had 30 times less TEP than Larson's and 3 times less than Rucks' Bh horizons. Phosphorus breakthrough in effluent for Dry Lake occurred earlier than those for Larson and Rucks. In spite of the large number of pore volumes displaced through all of the soil columns during both sorption and desorption experiments, the effluent concentration of P asymptotically approached but did not actually reach $C_0$ values. This behavior was especially accented with low $C_0$. Rao and Davidson (1979) found that pesticide BTC's measured in their research were asymmetrical in shape with extensive "tailing" when the relative concentration approached one or again at relative concentration of zero. The asymmetry of the BTC's for the pesticide was attributed to nonequilibrium (non-instantaneous reactions) conditions existing in the soil columns during flow or/and a nonlinearity in the adsorption/desorption process. The P BTC's obtained here from the Bh horizon soils, and in some cases the A horizon soils, showed similar behavior to that observed by Rao and Davidson (1979). Bottcher et al. (1986) and Selim et al. (1974) reported nonlinearity in phosphorus sorption isotherms for soil from A and Bh horizons of other Spodosols. This behavior was also presented in Chapter III and IV. Also, for a nonlinear isotherm, increasing the applied-P concentration leads to a non-proportional earlier breakthrough of P in the effluent due to the concentration dependence of the retardation, which was the case for the BTC for Bh horizon soil.

By calculating the area enclosed by $C/C_0 = 1.0$ and each experimental adsorption BTC and the area enclosed by the desorption BTC and $C/C_0 = 0.0$, the quantities of P adsorbed or desorbed in each soil column during the flow experiments were determined. The total amount of P applied, the amount of net adsorption or desorption of P, the ratio of net adsorption to total P applied, and the ratio of net

TABLE 5-3. Total quantities of P applied in solution and net amounts of P adsorbed and desorbed for each column.

| COLUMN # | TOTAL P APPLIED | NET P ADSORBED | NET P DESORBED | ADS/TOT* | DES/ADS** |
|---|---|---|---|---|---|
| | ---------(mg/kg)---------- | | | (%) | (%) |
| 1 | 1655.6 | 270.6 | 143.9 | 16.3 | 53.2 |
| 2 | 771.0 | 189.2 | 169.6 | 24.5 | 89.6 |
| 3 | 548.1 | 175.3 | 63.5 | 32.0 | 36.2 |
| 4 | 245.5 | 107.5 | 39.0 | 43.8 | 36.3 |
| 5 | 1629.4 | 190.0 | 80.9 | 11.7 | 42.6 |
| 6 | 985.4 | 151.6 | 58.8 | 15.4 | 38.8 |
| 7 | 350.7 | 97.2 | 27.5 | 27.7 | 28.3 |
| 8 | 264.6 | 77.5 | 25.6 | 29.3 | 33.0 |
| 9 | 1846.9 | 302.6 | 248.2 | 16.4 | 82.0 |
| 10 | 951.9 | 253.0 | 185.0 | 26.6 | 73.1 |
| 11 | 374.7 | 120.8 | 119.4 | 32.2 | 98.9 |
| 12 | 374.0 | 82.3 | 99.9 | 22.0 | 121.4 |

* Ratio between net absorption (ADS) and the total P applied (TOT) in percent

** Ratio between net desorption (DES) and the net P adsorbed (ADS) in percent desorption to adsorption for each soil column are shown in Table 5-3. For all three Bh horizons, the amount of P sorbed decreased with decreasing total P applied and the concentration of P applied. However, the percent of P sorbed increased with decreasing total P or concentration of P applied. These results reflect the nonlinear relationship between the solution and sorbed phases. For all three Bh horizons, the amount of P desorbed decreased as the total P applied ($C_0$) decreased or as the net P sorbed decreased. However, the percentage of P desorbed was influenced by the initial P concentration in the soil (MIP and TEP). The Bh horizon soil from the Larson dairy had the largest initial MIP and TEP concentrations and desorbed more P than the Bh horizon soils from Rucks and Dry Lake dairies. The ratio of the P sorbed to that desorbed was variable and decreased with decreasing $C_0$ for Rucks' and Dry Lake's Bh horizons and this behavior was inverted for Larson's. However, for 10 of the columns the ratio of P quantities desorbed were less than those sorbed. The higher variability in this set of data (DES/ADS) could be related the accumulative error from the adsorption experiments carried over to the calculation of the ratios. Fiskell and Mansell (1974) investigated the effect of rate of P application upon P sorption for a Spodosol. They found that as the application rate of P was increased, there was substantially less P retained. This result occurred because with increasing P application rate, the degree of saturation of P sorption sites increased and thus proportionately more P remained in solution. Berkheiser et al. (1980) concluded that low levels of phosphate application produced a relatively larger effect upon P sorbed per unit of added phosphate than high levels. This conclusion reflects the nonlinear distribution between P in solution and the P in sorbed phase. The soil of the Bh horizon collected at the Larson dairy showed a slightly larger net amount of P desorbed than soils from Rucks and Dry Lake dairies. The Larson soil desorbed more of the applied P, because the initial P content (Table 5-1) was larger than for soils from Rucks and Dry Lake. Furthermore, the amount of P adsorbed was not completely desorbed, which suggests that some of the P sorbed may have been irreversibly removed from solution. In the case of Larson Bh horizon, probably all the P sorbed could be desorbed which related initial P concentration and the amount of P desorbed and not to the amount of P sorbed. Although, the three Bh horizons sorbed the same amounts of P, only 50 % of these P amounts were desorbed for the soils that have the lowest initial P concentration (TEP). It was expected that in the case of Rucks and Dry Lake soils some of the adsorbed P would be irreversible (sink term), as was the observation obtained earlier by Mansell et al. (1977) for another Spodosol.

Table 5-4. Freundlich K and n values fitted to the column and batch data and the linear relationship between net amount of P sorbed by column vs batch data for a range of 1 to 100 mg P/l solution concentration.

| | RUCKS DAIRY | DRY LAKE DAIRY | LARSON DAIRY |
|---|---|---|---|
| COLUMN | | | |
| K (l/kg) | 80.95 | 48.61 | 40.86 |
| n | 0.253 | 0.291 | 0.447 |
| $r^2$ | 84.6 | 100.0 | 98.8 |
| BATCH | | | |
| K (l/kg) | 76.36 | 19.54 | 7.06 |
| n | 0.322 | 0.499 | 0.807 |
| $r^2$ | 96.1 | 93.2 | 89.7 |
| LINEAR RELATION | | | |
| intercept (mg P/kg) | 35.95 | 48.18 | 75.38 |
| slope | 0.672 | 0.734 | 0.899 |
| $r^2$ | 99.8 | 98.6 | 97.1 |

A Freundlich sorption isotherm was fitted to experimental data using the amount of P sorbed (Table 5-3) and the $C_0$ values (Table 5-2) for each soil column. The amount sorbed by the soil was assumed not to change significantly for greater numbers of pore volumes displaced through the column. Fitted K and n values as well as the correlation coefficients are shown in Table 5-4. The fitted values for K and n ranged from 40 to 80 l/kg and 0.25 to 0.45, respectively. The correlation coefficients were larger than 85%. The n values were directly related to the MIP and TEP values. However, the K values were not related to MIP and TEP, and the n and K values were not related to the percentage P sorbed or desorbed. The K and n values obtained from the column data were also compared with the K and n values fitted to batch study data for the same soils and initial P concentrations (Table 5-4). The K values obtained from the columns were larger and the n values were smaller than for the batch data. Both K and n values were likely influenced by difference in solution:soil ratios used for soil columns and batch experiments. Increasing the solution:soil ratio (approximately 0.3 and 25 ml/g solution:soil ratio for the column and batch study, respectively) should decrease the calculated K values. However, the ratio between column and batch K values were 10 to 100 times larger than that expected from the solution:soil ratio effect (0.3/25 = 0.012). The contact time of the columns was almost the same (24 h, for $C_0 = 100$ and 50 mg/l) or larger (48 to 96 h, for $C_0= 10$ and 5 mg/l) than the batch study, which excluded contact time as a factor affecting these results (Chapter IV, kinetic results). For an exponential (a power function,"n value") P sorption isotherm such as the Freundlich equation, the smaller the exponent (values of $n<1$ give a concave shape curve), the less the amount of P sorbed is dependent on concentration. Dry Lake's and Larson's Bh soil sorbed more P during application of P solutions to soil columns than in stirred batch studies, which explains the large difference between n values. Conversely, Rucks' Bh soil sorbed more P during batch than column investigations. However, the K and n values follow the same trend between column and batch, but the changes were not proportional. The K values decreased from Rucks to Larson and the n values increased from Rucks to Larson. The amount of P sorbed was calculated for equilibrium concentrations between 1 and 100 mg P/l using the fitted equation. The calculated values were compared by fitting a linear regression between column and batch calculated P sorbed data (Table 5-4). The correlation coefficients for all three soils were larger than 97%. The slope was less than one for all the Bh soils collected at Rucks, Dry Lake, and Larson dairies. It was observed from the linear regression that at a specific P concentration the amounts of P sorbed were the same for column and batch methods. The values for these specific concentration were approximately 3, 92, and 664 mg P/l for Rucks, Dry Lake, and Larson, respectively. Below that specific concentration, the soil during the batch study will sorb more P than during column conditions. Because the P concentration ranged between 5 and 100, soil from Dry Lake and Larson (below the specific concentration) under column conditions sorbed more than under batch conditions, and soil from Rucks (above the specific concentration) under batch conditions sorbed more P than under column conditions. However, the simple differences in solution:soil ratio will not explain the differences between column and batch conditions.

An unsaturated-unsteady solute transport model that assumes nonlinear, equilibrium sorption/desorption conditions (Mansell et al., 1989) was utilized to simulate water flow and P transport for the column experiments. The Rucks BTCs data for 10 and 100 mg P/l initial P concentrations were utilized for these comparisons. The K and n values calculated from the column experiments (Table 5-4) were utilized as parameters for the model. Figure 5-7 shows the difference between experimental data and the simulated line. Corresponding numbers of pore volumes of effluent for $C/C_0 = 0.5$ for the model and the data were almost the same. However, the P in the effluent solution appeared earlier, and the concentration never actually reached the initial P concentration even after 100 pore

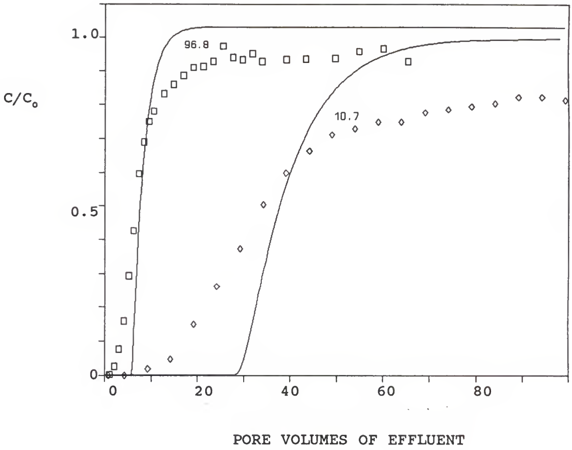


Figure 5-7. Comparing adsorption BTC curves for P in the effluent, from a soil column of Rucks Bh horizon with different $C_0$ applied (10 and 100 mg P/l), between the experimental data points and a simulated (Mansell et al., 1989) curve (solid line) using a transient transport model with local equilibrium and nonlinear sorption.

volumes as predicted with the model. Discrepancy between experimental and simulated BTC indicates that a nonlinear equilibrium model was not adequate to describe P sorption data. Nonlinear kinetics models have previously been shown (Mansell and Selim, 1981) to provide closer agreement with experimental results than simple equilibrium models.

## Conclusion

Phosphorus mobility was examined by displacing influent solutions containing 5, 10, 50, and 100 mg P/l $C_0$ through small columns of Bh soil horizons from three dairies located in the Okeechobee basin, and determining BTC's for P concentration in column effluent. The amount of P sorbed from the Bh soil horizons varied from site to site and was not related to the initial concentrations of P in the soils, as determined by Mehlich I or total extractions for P. The amount of P sorbed was strongly influenced by the P concentration of the influent applied. The larger the concentration of P applied, the larger the amount of P sorbed. However, the ratio between amount of P sorbed and total applied increased with a decrease in initial P applied, which reflects the nonlinear behavior observed in Chapter III and IV using batch studies between solution and sorbed phases. The amount of P desorbed following sorption was variable and no common trend was found. The P breakthrough curves (BTCs) for all the three sites' Bh horizons were very similar in shape and symmetry. A decrease in the initial concentration of P applied retarded the BTC's and resulted in a more gradual increase in P concentration in solution. The concentration of P applied ($C_0$) in the influent was never actually obtained in the outflow solution, and the relative difference between the in- and out-flow solutions was larger at low P concentrations. Freundlich sorption isotherm values for K and n were fitted to the column data and compared to the batch condition study data. The fitted values (K and n) were different for the column and batch conditions, and the differences could not be explained by the solution:soil ratio effect alone. The K and n fitted values, from column and batch conditions, could be used as an indicator of P sorption capacity for a specific soil.

# CHAPTER VI
# CONCLUSIONS

Eutrophication of Lake Okeechobee with phosphorus was found by earlier investigators (Chapter I) to be caused, mainly, by cow manure from dairy farming in the watershed north of the lake. Inorganic phosphorus or ortho-P was the most common form of phosphorus observed (Chapter I) in the manure and this form of P was utilized in the experiments presented in this dissertation. Indirect passage of P from the cow waste and wastewater to the drainage ditches and creeks will be influenced by the watershed soils and the water movement through them. More than 60% of the soils in the watershed have been previously classified as Spodosols. Spodosols have a dark subsurface horizon in which active, amorphous organic-sesquioxide materials have accumulated (spodic horizon or organic pan) within a matrix of quartz grains. All the dairies studied are located within areas of Spodosols. Ground-penetrating radar was utilized to investigate the variability of the spodic horizons (Chapter II). The results indicated that the spodic horizons were generally uniform, but the radar signal showed some discontinuity within the horizons. The surface of the Bh horizon was observed to mimic the surface contour, but not at the same gradient. This information indicates that spatial variability to the depth of the Bh horizon influence water and solute movement.

The status of the soils influenced by the dairy operations was investigated (Chapter III) by transect-sampling and three procedures for extracting soil P (water, Mehlich I, and total extractable). The information obtained indicated a large accumulation of P in the surface A horizon near the milking barn and close to the creek. However, the P concentration in the subsurface horizons were found to be similar between native, pasture, and holding area soils, indicating that much of the P did not move deeper in the profile in areas with high application of waste (holding areas). The sorption capacity of each of the soils sampled varied between horizons. The A and albic E horizons did not show any P sorption capacity with our experimental procedures. However, the Bh and C horizons exhibited variable sorption capacities. The high sorption capacity of the Bh horizon appeared to be related to the accumulation of highly reactive material (Al-organo complex). The high P concentration in the surface horizons near the milking barn was related to P precipitation with calcium as well as other cations coming from feed supplements and was complemented by high pH (around pH 7). No relationships were found between the sorption capacity of the horizons and the P extracted by either any of the three methods. This indicated that P is possibly retained as a precipitated form which did not influence, at the time scale of the experiment, the sorption capacity of the Bh or C horizons. Phosphorus precipitation in these horizons was shown to be related to aluminum or iron concentration in the soil and was complemented by a low pH of around 4. Information about the mineral characteristics, amorphous materials (imogolite), organic matter content, and aluminum and iron (total or exchangeable) for the soils that sorb P will be necessary in the future to determine the source of P sorption (adsorption-precipitation) sites for the Bh horizon and to complement P sorption and desorption data obtained here.

Kinetic data obtained at the same solution:soil ratio as that found under field conditions is highly desirable, but not obtained easily. Batch kinetics experiments, with a solution:soil ratio 10 to 100 times larger than field conditions, are still useful as an indicator for reaction rates of the P with the soil (Chapter IV). The results obtained, from a Bh horizon, indicated that the amount of P sorbed and the reaction rate increased with increasing initial concentration of P in solution (mg P/kg soil) and the amount of soil solids mass (decreasing solution:soil ratio) in contact with the initial solution. The kinetic data obtained were comparable with results from the published literature. The amount of sorbed P increased very fast initially and this "fast" reaction was completed within a half hour using stirred soil suspensions in aqueous solutions containing known concentrations of P. A "slow" sorption reaction followed the fast reaction and continued for 3 months for samples that had enough P in solution. Furthermore, the reaction rate decreased with time. These observations indicate that under field conditions P movement through the Bh horizon will be influenced by the travel or contact time and the concentration of the P-laden solution. Contact time is related to the velocity of water movement through the soil (pore water velocity), and during high water velocity, the contact time is smaller. Either or both high P concentration or short contact time was observed to facilitate the movement of P in these sandy soil. Information about the behavior of other cations and anions is helpful to understand the complex phenomena for P sorption. Calcium (Ca) and aluminum (Al) released by the soil were measured in the P-laden solution. Calcium was not influenced by contact time, which implied there was an exchange reaction between K and Ca, but was influenced by the amount of P sorbed by the soil. Phosphorus sorbed in a variable-charge soil such as Spodosols will tend to increase the CEC of the soil and decrease the amount of cations (Ca) in solution. However, Al was influenced by the contact time, which was related to mineral dissolution.

Column-flow investigation of P reaction with soil provides more realistic solutio:soil ratios but is more time consuming than simple batch studies. In spite of this, the amount of information obtained is required in order to investigate P sorption/desorption under field conditions. Care must be taken however, to differentiate between transport processes and reaction mechanisms or chemical reactions. The P sorption and desorption reaction (using a miscible displacement technique) with a Bh horizon packed in small columns was investigated (Chapter V) by applying P-laden solution of different concentrations ($C_o$). An increase in $C_o$ increased the mobility of the P during water flow. The shape of the BTCs observed exhibit characteristics typical of kinetics (nonequilibrium conditions) and nonlinearity, i.e. early breakthrough, clockwise rotation, and tailing. The relationship between the amount sorbed and in solution was nonlinear and describable by a Freundlich isotherm. However, the K and n values fitted to a Freundlich equation were smaller than the ones obtained by batch study, both with a large correlation coefficient value. The differences were only partially related to differences in solution:soil ratios between column and batch study conditions. A transport model assuming local equilibrium was compared to the BTC data using the K and n values obtained from the column study. As expected for an assumption of local equilibrium, the model overestimated retardation of P transport and thus did not represent the experimental data. Information about the effect of the velocity of the water movement through the column (pore water velocity) is an important asset in the understanding of P movement, due to the relationship between velocity (or contact time) and kinetics of P sorption. It was observed that the chemical and physical factors will influenced P behavior. A simple mathematical equation which includes sorption kinetics would be expected to greatly improve the description of P transport in these soils.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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